

Description

This invention relates to a coiled valve metal mesh for use, when uncoiled, as an electrode for electrochemical processes and to its method of manufacture.

5 The most important development in electrolysis electrodes in recent years has been the advent of dimensionally stable electrodes following the teachings of U.S. Patents No. 3,771,385 and 3,632,498. These dimensionally stable electrodes consists of a base or substrate of a valve metal, typically titanium, carrying an electrocatalytic coating such as a mixed oxide of platinum group metal and a valve metal forming a mixed crystal or solid solution. Many different coating formulations have been proposed.

10 The major use of these dimensionally stable electrodes has been as anodes in chlor-alkali production in mercury cells, diaphragm cells and more recently in membrane cells. Other uses have been as oxygen-evolving anodes for metal electrowinning processes, for hypochlorite and chlorate production, as metal plating anodes and so on. Use as an anode in cathodic protection has also been proposed and as cathodes in certain processes.

15 Platinized titanium anodes were already proposed as cathodic protection anodes and for other uses in US-A-3,278,404. The anodes, which could be of expanded titanium mesh, could also be of flexible form to be adapted to the requirements of cell design by bending. The examples for cathodic protection were in the form of rods.

20 Depending on the use, these dimensionally stable valve metal electrodes have been proposed with various configurations such as rods, tubes, plates and complex structures such as an array of rods or blades mounted on a supporting current conducting assembly as well as a mesh of expanded valve metal typically having diamond shaped voids mounted on a supporting current conducting assembly which provides the necessary rigidity.

25 Electrodes in the form of platinized valve metal wire are known for cathodic protection, but in practically every other application rigidity and dimensional stability of the electrode are critical factors for successful operation. For example, many electrolytic cells are operated with an inter-electrode gap of only a few millimeters and the flatness and rigidity of the operative electrode face are extremely important.

30 For most applications, the dimensionally stable electrodes operate at relatively high current densities, typically 3-5 KA/m² for membrane cells, 1-3 KA/m² for diaphragm cells and 6-10 KA/m² for mercury cells. These high current densities, combined with the requirements of planarity/rigidity, necessitate valve metal structures of substantial current carrying capacity and strength.

35 Typical known valve metal electrodes of the type with expanded titanium mesh as operative face use a mesh having an expansion factor of 1.5 to 4 times providing a void fraction of about 30 to 70 percent. Such titanium sheets may be slightly flexible during the manufacturing processes but the inherent elasticity of the sheet is restrained, e.g. by welding it to a current conductive structure, typically having one or more braces extending parallel to the SWD dimension of the diamond-shaped openings. Such electrode sheets typically have a current-carrying capacity of 2-10 KA/m² of the electrode surface.

Other electrode configurations are known for special purposes, e.g., a rigid cylindrical valve metal sheet mounted in a linear type of anode structure for cathodic protection (see U.S. patent No. 4,515,886).

40 Manufacture of the known electrodes usually involves assembly of the electrode valve metal structure, e.g. by welding, followed by surface treatment such as degreasing/etching/sandblasting and application of the electrocatalytic coating by various methods including chemi-deposition, electroplating and plasma spraying. Chmi-deposition may involve the application of a coating solution to the electrode structure by dipping or spraying, followed by baking usually in an oxidizing atmosphere such as air.

45 Summary of the Invention

It has now been found that titanium and other valve metals, e.g., tantalum and zirconium, can be greatly expanded to a pattern of substantially diamond-shaped voids having an extremely high void fraction. Having been expanded in this way material cost becomes acceptable and they form an ideal structure for cathodic protection. Moreover the greatly expanded mesh is flexible and coilable and uncoilable about an axis along the LWD dimension. Thus the expanded metal can be supplied in the form of large rolls which can be easily unrolled onto a surface to be protected, such as a concrete deck or a concrete substructure. The pattern of voids in the mesh is defined by a continuum of valve metal strands interconnected at nodes and carrying on their surface an electrocatalytic coating. These multiplicity of strands provide redundancy for current flow in the event that one or more strands become broken during shipping or installation. The metal mesh is stretchable along the SWD dimension of the pattern units whereby a coiled electrode roll of the mesh can be uncoiled on, and stretched over, a supporting substrate and into an operative electrode configuration.

60 The electrode mesh of the present invention satisfies all of the requirements for use in cathodic protection of reinforcing steel in concrete. It consists of a coil of the highly expanded valve metal activated by an electrocatalytic coating, and which can be uncoiled for use. Current can be distributed to the expanded valve metal by a welded contact of the same valve metal. A multitude of current paths in the expanded metal structure provide for redundancy of current distribution and hence the distribution of current to the reinforcing steel is excellent. Installation is simple since an electrode of greater than 100 square meters can be quickly rolled onto the surface of a concrete deck or easily cut to size and wrapped

around a concrete substructure. However, generally the coated mesh of the present invention may be utilized in any operation wherein the electrocatalytic coating on a valve metal substrate will be useful and wherein current density operating conditions up to 10 amps per square meter of mesh area are contemplated. Further details of the aspect of cathodic protection in concrete and the installation of coated mesh for such protection are provided in concurrently filed Application Number 86903075.9 (WO86/06759).

The electrocatalytic coating used in the present invention is such that the anode operates at a very low single electrode potential, and may have a life expectancy of greater than 20 years in a cathodic protection application. Unlike other anodes used heretofore for the cathodic protection of steel in concrete, it is completely stable dimensionally and produces no carbon dioxide or chlorine from chloride contaminated concrete. It furthermore has sufficient surface area such that the acid generated from the anodic reaction will not be detrimental to the surrounding concrete.

In a broad aspect, the present invention is directed to a coiled valve metal mesh for use when uncoiled as electrode for electrochemical processes, the valve metal mesh having a pattern substantially diamond-shaped voids having long way of design (LWD) and short way of design (SWD) dimensions for units of the pattern, the pattern of voids being defined by a continuum of valve metal strands interconnected at nodes and carrying on their surface an electrochemically active coating. The mesh of valve metal is a flexible and stretchable mesh with strands of thickness less than 0.125cm and having a void fraction of at least 90%. The flexible mesh is coilable and uncoilable about an axis along the LWD dimension of the pattern units and is stretchable when uncoiled by up to about 10% along the SWD dimension of the pattern units and further is bendable in the general plane of the mesh about a bending radius in the range of from 5 to 25 times the width of the mesh, whereby the electrode mesh can be uncoiled onto a supporting surface on which the mesh can be stretched to an operative electrode configuration.

Also the present invention is directed to a fast and economical coating technique for coiled mesh even of greatly extended length. Such technique can achieve highly suitable coating results without deleterious strand breakage even for the more delicate meshes of greatly expanded valve metal and which have extremely great void volume. Compared to prior art techniques for producing coated valve metal electrodes, considerably greater electrode areas, for instance about 100 or even 200 square meters or even greater electrode surface areas, can be coated as a continuous expanse. Moreover, this economical coating operation can be undertaken and completed with equipment that typically will be readily available in existing facilities having conventional coating apparatus.

In this coating aspect, the present invention thus pertains to a method of manufacturing a coiled valve metal mesh for use when uncoiled as an electrode for electrochemical processes of the type comprising a valve metal mesh provided with a pattern of substantially diamond shaped voids having LWD and SWD dimensions for units of the pattern, the pattern of voids being defined by a continuum of thin valve metal strands interconnected at nodes and carrying on their surface an electrocatalytic coating, with the method comprising:

- (a) providing a flexible, coiled valve metal mesh, the mesh being as described hereinabove and being coiled about an axis along the direction of the LWD dimension of the pattern, and
- (b) applying an electrocatalytic coating to the surface of the valve metal mesh while same is coiled to provide a flexible coated electrode mesh in coiled configuration for use when uncoiled as an electrode.

The present invention is also directed to the use of the mesh, in uncoiled configuration, as an electrode.

Brief Description of the Drawings

FIGURE 1 shows a diamond-shaped unit of a greatly expanded valve metal mesh of the present invention.

FIGURE 2 shows a section of greatly expanded valve metal mesh, embodying diamond-shaped structure, and having a current distributor along the LWD dimension and welded to mesh nodes.

FIGURE 3 is an enlarged view of a mesh node, particularly showing the node double strand thickness.

Description of the Preferred Embodiments

The metals of the valve metal mesh will most always be any of titanium, tantalum, zirconium and niobium. As well as the elemental metals themselves, the suitable metals of the mesh can include alloys of these metals with themselves and other metals as well as their intermetallic mixtures. Of particular interest for its ruggedness, corrosion resistance and availability is titanium. Where the mesh will be expanded from a metal sheet, the useful metal of the sheet will most always be an annealed metal. As representative of such serviceable annealed metals is Grade I titanium, an annealed titanium of low embrittlement. Such feature of low embrittlement is necessary where the mesh is to be prepared by expansion of a metal sheet, since such sheet should have an elongation of greater than 20 percent. This would be an elongation as determined at normal temperature, e.g., 20°C., and is the percentage elongation as determined in a two-inch (5 cm.) sheet of greater than 0.025 inch (.0635 cm.) thickness. Metals for expansion having an elongation of less than 20 percent will be too brittle to insure suitable expansion to useful mesh without deleterious strand breakage.

Advantageously for enhanced freedom from strand breakage, the metal used in expansion will have an elongation of at least about 24 percent and will virtually always have an elongation of not greater than

about 40 percent. Thus metals such as aluminum are neither contemplated, nor are they useful, for the mesh in the present invention, aluminum being particularly unsuitable because of its lack of corrosion resistance. Also with regard to the useful metals, annealing may be critical as for example with the metal tantalum where an annealed sheet can be expected to have an elongation on the order of 37 to 40 percent, which metal in unannealed form may be completely useless for preparing the metal mesh by having an elongation on the order of only 3 to 5 percent. Moreover, alloying may add to the embrittlement of an elemental metal and thus suitable alloys may have to be carefully selected. For example, a titanium-palladium alloy, commercially available as Grade 7 alloy and containing on the order of 0.2 weight percent palladium, will have an elongation at normal temperature of above about 20 percent and is expensive but could be serviceable, particularly in annealed form. Moreover, where alloys are contemplated, the expected corrosion resistance of a particular alloy that might be selected may also be a consideration. For example, in Grade 1 titanium, such is usually available containing 0.2 weight percent iron. However, for superior corrosion resistance, Grade 1 titanium is also available containing less than about 0.05 weight percent iron. Generally, this metal of lower iron content will be preferable for many applications owing to its enhanced corrosion resistance.

The metal mesh may then be prepared directly from the selected metal. For best ruggedness in extended metal mesh life, it is preferred that the mesh be expanded from a sheet or coil of the valve metal. It is however contemplated that alternative meshes to expanded metal meshes may be serviceable. For such alternatives, thin metal ribbons can be corrugated and individual cells, such as honeycomb shaped cells can be resistance welded together from the ribbons. Slitters or corrugating apparatus could be useful in preparing the metal ribbons and automatic resistance welding could be utilized to prepare the large void fraction mesh. By the preferred expansion technique, a mesh of interconnected metal strands can directly result. Typically where care has been chosen in selecting a metal of appropriate elongation, a highly serviceable mesh will be prepared using such expansion technique with no broken strands being present. Moreover with the highly serviceable annealed valve metals having desirable ruggedness coupled with the requisite elongation characteristic, some stretching of the expanded mesh can be accommodated during installation of the mesh. This can be of particular assistance where uneven substrate surface or shape will be most readily protected by applying a mesh with such stretching ability. Generally a stretching ability of up to about 10 percent can be accommodated from a roll of Grade 1 titanium mesh having characteristics such as discussed hereinbelow in the example. Moreover the mesh obtained can be expected to be bendable in the general plane of the mesh about a bending radius in the range of from 5 to 25 times the width of the mesh.

Where the mesh is expanded from the metal sheet, the interconnected metal strands will have a thickness dimension corresponding to the thickness of the initial planar sheet or coil. Usually this thickness will be within the range of from about 0.05 centimeter to about 0.125 centimeter. Use of a sheet having a thickness of less than about 0.05 centimeter, in an expansion operation, can not only lead to a deleterious number of broken strands, but also can produce a too flexible material that is difficult to handle. For economy, sheets of greater than about 0.125 centimeter are avoided. As a result of the expansion operation, the strands will interconnect at nodes providing a double strand thickness of the nodes. Thus the node thickness will be within the range of from about 0.1 centimeter to about 0.25 centimeter. Moreover, after expansion the nodes for the special mesh will be completely, to virtually completely, non-angulated. By that it is meant that the plane of the nodes through their thickness will be completely, to virtually completely, vertical in reference to the horizontal plane of an uncoiled roll of the mesh.

In considering the preferred valve metal titanium, the weight of the mesh will usually be within the range of from about 0.05 kilogram per square meter to about 0.5 kilogram per square meter of the mesh. Although this range is based upon the exemplary metal titanium, such can nevertheless serve as a useful range for the valve metals generally. Titanium is the valve metal of lowest specific gravity. On this basis, the range can be calculated for a differing valve metal based upon its specific gravity relationship with titanium. Referring again to titanium, a weight of less than about 0.05 kilogram per square meter of mesh will be insufficient for proper current distribution in enhanced cathodic protection. On the other hand, a weight of greater than about 0.5 kilogram per square meter will most always be uneconomical for the intended service of the mesh.

The mesh can then be produced by expanding a sheet or coil of metal of appropriate thickness by an expansion factor of at least 10 times, and preferably at least 15 times. Useful mesh can also be prepared where a metal sheet has been expanded by a factor up to 30 times its original area. Even for an annealed valve metal of elongation greater than 20 percent, an expansion factor of greater than 30:1 may lead to the preparation of a mesh exhibiting strand breakage. On the other hand, an expansion factor of less than about 10:1 may leave additional metal without augmenting cathodic protection. Further in this regard, the resulting expanded mesh should have an at least 80 percent void fraction for efficiency and economy of cathodic protection. Most preferably, the expanded metal mesh will have a void fraction of at least about 90 percent, and may be as great as 92 to 96 percent or more, while still supplying sufficient metal and economical current distribution. With such void fraction, the metal strands can be connected at a multiplicity of nodes providing a redundancy of current-carrying paths through the mesh which insures effective current distribution throughout the mesh even in the event of possible breakage of a number of individual strands, e.g., any breakage which might occur during installation or use. Within the expansion

factor range as discussed hereinbefore, such suitable redundancy for the metal strands will be provided in a network of strands most always interconnected by from about 500 to about 2000 nodes per square meter of the mesh. Greater than about 2000 nodes per square meter of the mesh is uneconomical. On the other hand, less than about 500 of the interconnecting nodes per square meter of the mesh may provide for

insufficient redundancy in the mesh. Within the above-discussed weight range for the mesh, and referring to a sheet thickness of between about 0.05—0.125 centimeter, it can be expected that strands within such thickness range will have width dimensions of from about 0.05 centimeter to about 0.20 centimeter. For the special application to cathodic protection in concrete, it is expected that the total surface area of interconnected metal, i.e., including the total surface area of strands plus nodes, will provide between about 10 percent up to about 50 percent of the area covered by the metal mesh. Since this surface area is the total area, as for example contributed by all four faces of a strand of square cross-section, it will be appreciated that even at a 90 percent void fraction such mesh can have a much greater than 10 percent mesh surface area. This area will usually be referred to herein as the "surface area of the metal" or the "metal surface area". If the total surface area of the metal is less than about 10 percent; the resulting mesh can be sufficiently fragile to lead to deleterious strand breakage. On the other hand, greater than about 50 percent surface area of metal will supply additional metal without a commensurate enhancement in protection.

After expansion the resulting mesh can be readily rolled into coiled configuration, such as for storage or transport or further operation. With the representative valve metal titanium, rolls having a hollow inner diameter of greater than 20 centimeters and an outer diameter of up to 150 centimeters, preferably 100 centimeters, and usually not substantially above about 50 centimeters can be prepared. These rolls can be suitably coiled from the mesh when such is prepared in lengths within the range of from about 40 to about 200, and preferably up to 100, meters. For the metal titanium, such rolls will have weight on the order of about 10—50 kilograms, but usually below 30 kilograms to be serviceable for handling, especially following coating, and particularly handling in the field during installation for cathodic protection.

In such greatly expanded valve metal mesh it is most typical that the gap patterns in the mesh will be formed as diamond-shaped apertures. Such "diamond-pattern" will feature apertures having a long way of design (LWD) from about 4, and preferably from about 6, centimeters up to about 9 centimeters, although a longer LWD is contemplated, and a short way of design (SWD) of from about 2, and preferably from about 2.5, up to about 4 centimeters. In the preferred application of cathodic protection in concrete, diamond dimensions having an LWD exceeding about 9 centimeters may lead to undue strand breakage and undesirable voltage loss. An SWD of less than about 2 centimeters, or an LWD of less than about 4 centimeters, in the preferred application, can be uneconomical in supplying an unneeded amount of metal for desirable cathodic protection.

Referring now more particularly to Fig. 1 an individual diamond shape, from a sheet containing many such shapes is shown generally at 2. The shape is formed from strands 3 joining at connections (nodes) 4. As shown in the Figure, the strands 3 and connections 4 form a diamond aperture having a long way of design in a horizontal direction. The short way of design is in the opposite, vertical direction. When referring to the surface area of the interconnected metal strands 3, e.g., where such surface area will supply not less than about 10 percent of the overall measured area of the expanded metal as discussed hereinabove, such surface area is the total area around a strand 3 and the connections 4. For example, in a strand 3 of square cross-section, the surface area of the strand 3 will be four times the depicted, one-side-only, area as seen in the Figure. Thus in Fig. 1, although the strands 3 and their connections 4 appear thin, they may readily contribute 20 to 30 percent surface area to the overall measured area of the expanded metal. In Fig. 1, the "area of the mesh", e.g., the square meters of the mesh, as such terms are used herein, is the area encompassed within an imaginary line drawn around the periphery of the mesh.

In Fig. 1, the area within the diamond, i.e., within the strands 3 and connections 4, may be referred to herein as the "diamond aperture". It is the area having the LWD and SWD dimensions. For convenience, it may also be referred to herein as the "void", or referred to herein as the "void fraction", when based upon such area plus the area of the metal around the void. As noted in Fig. 1 and as discussed hereinbefore, the metal mesh as used herein has extremely great void fraction. Although the shape depicted in the figure is diamond-shaped, it is to be understood that many other shapes can be serviceable to achieve the extremely great void fraction, e.g., scallop-shaped or hexagonal.

Referring now to Fig. 2, several individual diamonds 21 are formed of individual strands 22 and their interconnections 25 thereby providing diamond-shaped apertures. A row of the diamonds 21 is bonded to a metal strip 23 at the intersections 25 of strands 22 with the metal strip 23 running along the LWD of the diamond pattern. The assembly is brought together by spotwelds 24, with each individual strand connection (node) 25 located under the strip 23 being welded by a spotweld 24. Generally the welding employed will be electrical resistance welding and this will most always simply be spot welding, for economy, although other, similar welding technique, e.g., roller welding, is contemplated. This provides a firm interconnection for good electroconductivity between the strip 23 and the strands 22. As can be appreciated by reference particularly to Fig. 2, the strands 22 and connections 25 can form a substantially planar configuration. As such term is used herein it is meant that particularly larger dimensional sheets of the mesh may be generally in coiled or rolled condition, as for storage or handling, but are capable of being unrolled into a "substantially planar" condition or configuration, i.e., substantially flat form, for use.

Moreover, the connections 25 will have double strand thickness, whereby even when rolled flat, the substantially planar or flat configuration may nevertheless have ridged connections.

Referring then to the enlarged view in FIG. 3, it can be seen that the nodes have double strand thickness (2T). Thus, the individual strands have a lateral depth or thickness (T) not to exceed about 0.125 centimeter, as discussed hereinabove, and a facing width (W) which may be up to about 0.20 centimeter.

The expanded metal mesh can be usefully coated. It is to be understood that the mesh may also be coated before it is in mesh form, or combinations might be useful. Whether coated before or after being in mesh form, the substrate can be particularly useful for bearing a catalytic active material, thereby forming a catalytic structure. As an aspect of this use, the mesh substrate can have a catalyst coating, resulting in an anode structure.

The metal, including coiled metal mesh, before electrocatalytic coating operation, may proceed through one or more of various pretreatment procedures. Such procedures may be simplistic, for example a simple rinse operation. Not infrequently the mesh may have, e.g., as by being imparted from the expansion operation, oils or other surface contamination. Therefore, a suitable pretreatment technique will often include a solvent degreasing operation. This can most always be accomplished with typical halocarbon solvent such as the chlorinated and/or fluorinated solvents as represented by chlorotrifluoromethane, methylene chloride and perchloroethylene. Other pretreatments for the coiled metal mesh may include the further typical techniques such as pickling and etching, as well as dry honing, i.e., sand blasting. In dry honing, a gritty and very finely divided, hard particulate can be blasted at the coiled mesh at high velocity. In a representative etching operation most usually an aqueous solution of inorganic acid will be used to contact the metal mesh as by spray or dip contact. Generally a strong inorganic acid aqueous solution, e.g., hydrochloric acid at a strength of up to about 30 percent concentration or more, can be utilized. It is also contemplated that combination pretreatment techniques may be employed. Such combination operations can include not only those where two different steps for a single operation are useful, e.g., a combination of spray and dip technique for degreasing, but also a combination such as a washing or rinsing action combined with mild abrasive treatment. Where several pretreatment operations are employed, for example degreasing and etching, intermediate steps between each operation may be used, such as drying and/or rinsing steps and the like.

It will be most suitable to pretreat the valve metal mesh from typical expansion operation by first degreasing, as in a commercial degreaser containing a boiling halocarbon solvent, e.g., perchloroethylene and then follow the degreasing by etching. This etching may include contact with an aqueous, concentrated hydrochloric acid solution, as by dip coating contact for a time up to about 20 minutes. A contact time of greater than about 20 minutes can lead to deleterious loss of metal in the etching operation. Usually the coiled metal mesh will be dipped into the etching solution for a time of at least about 5 minutes to provide sufficient metal surface roughness for enhanced coating adhesion and distribution. The useful concentrated hydrochloric acid solutions can contain acid in an amount within the range from about 5 to about 30 percent.

The liquid coating composition used will be such an electrochemically active coating as can be useful when applied as a lightweight coating. This lightweight coating, or "low loading" coating will often be at a coating weight of less than about 0.5 gram of platinum group metal per square meter of the metal mesh substrate. On the other hand some coatings will be useful when present in an amount of as little as about 0.05 gram of platinum metal per square meter of a metal mesh substrate. As representative of the electrochemically active coatings are those provided from platinum or other platinum group metals or they can be represented by active oxide coatings such as platinum group metal oxides, magnetite, ferrite, cobalt spinel or mixed metal oxide coatings. Such coatings have typically been developed for use as anode coatings in the industrial electrochemical industry. Suitable coatings of this type have been generally described in one or more of the U.S. Patents 3,265,526, 3,632,498, 3,711,385 and 4,528,084. The mixed metal oxide coatings can often include at least one oxide of a valve metal with an oxide of a platinum group metal including platinum, palladium, rhodium, iridium and ruthenium or mixtures of themselves and with other metals. It is preferred for economy that the low load electrocatalytic coatings be such as have been disclosed in the U.S. Patent No. 4,528,084.

It is contemplated that coatings will be applied to the coiled metal mesh by any of those means which are useful for applying a liquid coating composition to a metal substrate. Such methods include dip spin and dip drain techniques. Moreover spray application and combination techniques, e.g., dip drain with spray application can be utilized. With the above-mentioned coating compositions for providing an electrochemically active coating, a modified dip drain operation of the coiled metal mesh will be most serviceable. In this operation, the coil will be dipped into a bath of coating composition in a manner whereby the axis through the hollow center of the coil is at least substantially parallel to the surface of the liquid coating composition. The coil can be partly immersed or completely submersed in the coating composition. During contact it is then preferred to rotate the coil around its central axis to provide for thorough and even distribution of the liquid coating composition on the metal substrate. Particularly where large rolls of coiled metal are coated, this technique is preferable as only partial immersion of the coil in the coating solution is needed, with the subsequent rolling operation providing for thorough wetting out of the coating composition on the mesh substrate. To enhance such coating operation, the coil may be immersed and rotated, withdrawn from the coating composition bath, and then reimmersed and rotated, or counter-

rotated, with such operation being repeated to thoroughly coat the coiled mesh. In alternative processing, the hollow center of the coil can be vertical and the coil hung in this manner is then either partially or completely dipped, i.e., up to total coil immersion, in the coating composition. Following any of the foregoing coating procedures, upon removal from the liquid coating composition, the wet coil may simply dip drain or be subjected to other post coating technique such as forced air drying.

Typical curing conditions for the electrocatalytic coating can include cure temperatures of from about 300°C. up to about 600°C. Curing times may vary from only a few minutes for each coating layer up to an hour or more, e.g., a longer cure time after several coating layers have been applied. The curing operation can be any of those that may be used for curing a coating on a metal substrate. Thus, oven curing, including conveyor ovens may be utilized. Moreover, infrared cure techniques can be useful. Preferably for most economical curing, oven curing is used and the cure temperature used will be within the range of from about 450°C. to about 550°C. At such temperatures, curing times of only a few minutes, e.g., from about 3 to 10 minutes, will most always be used for each applied coating layer.

It has been found that the coils of greatly expanded mesh, although being lightweight, are nevertheless difficult to handle since sharp mesh edges can make manual handling hazardous. The coating is thus particularly suitable for reducing injury in the manual handling operations associated with the coiled mesh. For facilitating the manual handling ease of the mesh, as when a coil is placed into or removed from storage or when proceeding to subsequent operation, such as assembling with other elements, the coating readily lends itself to assisting in this ease of handling. And such is especially desirable as in the case of providing the electrochemically lightweight active coating as this will not thereafter interfere with subsequent electrical resistance welding. Thus, the above-described coating operation can be utilized following coiled mesh production whereby the resulting coated article can not only proceed to subsequent processing operation, but will also lend itself to ready manual handling in such operation.

In utilizing the coiled mesh it will often be desirable to affix additional metal members to the mesh, such as after coating. For example, metal current distributor members can be metallurgically bonded to the coated coil. Attachment of additional metal members can occur following the coating operation. Although various metallurgical bonding techniques for assembling the coated roll with additional metal elements are contemplated, it has been found that electrical resistance welding can be efficiently employed. Thus, where the additional metal elements include current distribution members, these can be utilized as strips applied to the unrolled mesh and the strips can be spot welded across the mesh at the nodes. Furthermore, in such an assembly the current distributor members can have the low loading of electrocatalytic coating. Electrical resistance welding can be successfully employed to prepare these coated metal assemblies even where the metals for welding in face-to-face contact will each be coated faces. Such current distributor member can then connect outside of the concrete environment to a current conductor, which current conductor being external to the concrete need not be so coated. For example in the case of a concrete bridge deck, the current distribution member may be a bar extending through a hole to the underside of the deck surface where a current conductor is located. In this way all mechanical current connections are made external to the finished concrete structure, and are thereby readily available for access and service if necessary. Connections to the current distribution bar external to the concrete may be of conventional mechanical means such as a bolted spade-lug connector.

Application of the coated mesh for corrosion protection such as to a concrete deck or substructure can be simplistic. A roll of the greatly expanded valve metal mesh with a suitable electrochemically active coating, sometimes referred to hereinafter simply as the "anode", can be unrolled onto the surface of such deck or substructure. Thereafter, means of fixing mesh to substructure can be any of those useful for binding a metal mesh to concrete that will not deleteriously disrupt the anodic nature of the mesh. Usually, non-conductive retaining members will be useful. Such retaining members for economy are advantageously plastic and in a form such as pegs or studs. For example, plastics such as polyvinyl halides or polyolefins can be useful. These plastic retaining members can be inserted into holes drilled into the concrete. Such retainers may have an enlarged head engaging a strand of the mesh under the head to hold the anode in place, or the retainers may be partially slotted to grip a strand of the mesh located directly over the hole drilled into the concrete.

Usually when the anode is in place and while held in close contact with the concrete substructure by means of the retainers, an ionically conductive overlay will be employed to completely cover the anode structure. Such overlay may further enhance firm contact between the anode and the concrete substructure. Serviceable ionically conductive overlays include portland cement and polymer-modified concrete.

In typical operation, the anode can be overlaid with from about 2 to about 6 centimeters of a portland cement or a latex modified concrete. In the case where a thin overlay is particularly desirable, the anode may be generally covered by from about 0.5 to about 2 centimeters of polymer modified concrete. The expanded valve metal mesh substrate of the anode provides the additional advantage of acting as a metal reinforcing means, thereby improving the mechanical properties and useful life of the overlay. It is contemplated that the metal mesh anode structure will be used with any such materials and in any such techniques as are well known in the art of repairing underlying concrete structures such as bridge decks and support columns and the like.

The following examples show ways in which the invention has been practiced, but should not be construed as limiting the invention.

Example 1

5 An imperforate sheet of Grade I titanium 100 centimeter (cm) wide $\times$ 300 cm long $\times$ 0.889 millimeter (mm) thick (T), and having an elongation at 68°C. of 24 percent for a 2-inch (5 cm.) sheet greater than 0.025 inch (0.0635 cm.) thick, was expanded to a diamond pattern. The dies doing the piercing of the sheet also acted as forming dies to expand the punched slits into the diamond-shaped openings. The process employed a punch with a full indexing to one side to complete the design. Each diamond measured 7.62 cm
10 LWD $\times$ 3.38 cm SWD. Expansion factor was 19 to 1, e.g., a test sheet 160 cm. long was expanded during the patterning to approximately 30.5 m, providing a void fraction of 95 percent. The final strand dimension was 0.889 mm (T) $\times$ 0.914 mm (W). Expansion was at a rate of 220 strokes per minute with no broken strands. The finished expanded titanium had a weight of 0.20 kilogram (Kg) per square meter (m²) of the resulting mesh and an actual metal surface area (strands plus nodes) of 0.23 m² per square meter of the resulting
15 mesh. The 30.5 m long mesh was conveniently stored and handled in rolled configuration.

A current distribution bar was spot welded to one end of a piece of the expanded titanium, taken from the unrolled mesh, which measured 30 cm $\times$ 38 cm. The structure was next vapor degreased in perchloroethylene vapor and etched in a 20 weight percent HCl solution for 5 minutes. It was thereafter water rinsed and steam dried. It was then coated with mixed oxides of titanium and ruthenium in which the
20 ruthenium content was 0.35 gram per square meter. Anodes prepared in this manner were subjected to accelerated life testing at high current density in 1.0 M H₂SO₄. An anode at 300,000 (3 $\times$ 10⁵) milliamps (mA) per square meter failed after 7.5 hours, and an anode at 100,000 (1 $\times$ 10⁵) mA per square meter failed after 82 hours under these conditions. Using known relationships between current density and anode lifetime, these results extrapolate to an expected life of over 200 years at a practical current density of 100 mA per
25 square meter of the metal surface area of the expanded titanium.

An anode prepared as described above is then placed on top of a chloride contaminated concrete block and overlaid with 50 mm thickness of portland cement. A second identical anode is also placed on top of a chloride contaminated concrete block and overlaid with a 38 mm thickness of latex modified concrete. Both structures are judged by visual inspection to have desirable interbonding of the cement to concrete for the
30 one block and of the modified concrete to concrete for the second block. From the hereinabove described accelerated life tests, lifetimes of anodes in these blocks are therefore expected to be very long.

Example 2

35 An imperforate coil of Grade I titanium 114 centimeters (cm) wide $\times$ 1.69 meters (m) long $\times$ 0.635 millimeter (mm) thick, and having an elongation at 68°C. of 24 percent (for a 2-inch (5cm.) sheet greater than 0.025 inch (0.0635 cm.) thick), was expanded to a diamond pattern in the manner described in Example 1. Each unit diamond of the pattern measured 7.62 cm LWD $\times$ 3.38 cm SWD. Expansion factor was 27 to 1, e.g., the test sheet 1.69 m long was expanded during the patterning to approximately 45.7 m, providing a void fraction of 96 percent. The final strand dimension was 0.635 mm $\times$ 0.736 mm. Expansion was at a rate
40 of 220 strokes per minute with no broken strands. The finished expanded titanium had a weight of 0.12 kilogram (Kg) per square meter (m²) of the resulting mesh and an actual metal surface area (strands plus nodes) of 0.16 m² per square meter of the resulting mesh.

The expanded metal coming through the expansion apparatus was easily coiled into a roll. The resulting roll had an approximately 30 cm diameter interior hollow zone and an overall outside diameter of
45 about 40 cm. The weight of the roll was approximately 11.8 kilos. Titanium metal tie wires were used to prevent the roll from uncoiling in further operation. A support rod was passed through the central hollow zone of the roll and the rod extended beyond the roll at each end whereby lines attached to each end from overhead were used with lifting apparatus. By means of this support rod assembly the roll was then lowered into a degreasing machine containing boiling perchloroethylene solvent. The roll was retained in the overhead vapor zone for about 20 minutes. Thereafter, again by use of the support rod assembly, the
50 degreased coil was immersed for 10 minutes in an aqueous solution of 20 weight percent hydrochloric acid, which solution was maintained at 95°C. Following this etching operation the coil was removed from the etching solution, water rinsed for about 15 minutes followed by steam drying for about 20 minutes.

Again by way of the support rod assembly, the coil was then dipped into a bath of coating solution for providing an electrochemically active coating on the coil. Coating solutions such as the one of this bath fall under the U.S. Patent No. 3,632,498, example 1. Since this depth of coating solution was less than the diameter of the coil, the coil was slowly rotated to expose the entire coil to the coating solution. Furthermore, the coil was lifted from the solution, rotated slightly around the support rod, redipped into the coating solution and rerolled through the solution. Upon final removal from the coating solution, the coil
60 was agitated by a light manual shaking and then was retained over the tank of coating solution for approximately 30 minutes to permit solution that has been temporarily retained in corners of the diamond-shaped units to drain, as well as to permit the coil to dry.

The dried coil was maintained on its support rod apparatus and by means of this support was then introduced to a conveyor oven. The coil proceeded through the oven in a time of 4 minutes whereby the
65 wire mesh facing the hollow central zone of the coil attained a temperature of approximately 500°C. Upon

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removal from the oven, the coil was reconveyed for a second 4 minute pass through the oven. After the second pass, the coil is permitted to cool. It was then subsequently uncoiled and found to contain no broken strands or adjacent strands stuck together by such coating and curing operation, and thus was easily and completely uncoiled.

5 In analysis of coils coated in this manner, wherein the coils have been uncoiled and test pieces cut out for analysis, the coating has been found to provide mixed oxides of titanium and ruthenium in which the ruthenium content is 0.35 gram per square meter. Furthermore, such coating has been found to be sufficiently distributed throughout the mesh that all randomly selected areas for analysis demonstrate desirable coating content. Anodes prepared from such randomly selected samples and subjected to
10 accelerated life testing have all demonstrated enhanced performance sufficient for these mesh anodes to serve in cathodic protection, such as protection of steel reinforced concrete. The coating and curing process using the mesh in coiled form, is thus judged to be highly desirable for supplying coated mesh which will be serviceable as such anodes.

As illustrative of exemplary meshes which can be or have been useful, there are presented the
15 following:

Mesh Specifications

Type 1 Mesh

20	Composition	Titanium Grade 1
	Width of Roll	45 inches (112.5 cm)
25	Length	250 to 500 ft. (75 to 150 m)
	Weight	26 lbs./1000 ft. ² (11.7 kg/100m ²)
30	Diamond Dimension	3" LWD × 1 1/3" SWD (7.6 cm LWD × 3.3cm SWD)
	Resistance Lengthwise (45 inch/112.5 cm wide)	.026 ohm/ft. (0.086 ohm/m)
35	Resistance Widthwise with Current Distributor	.007 ohm/ft. (0.02 ohm/m)
	Bending Radius	3/32 inches (0.24 cm)
40	Bending Radius in Mesh Plane	50 ft. (15 m)

Type 2 Mesh

45	Composition	Titanium Grade 1
	Width of Roll	4 ft. (122 cm)
	Length	250 to 500 ft. (75 to 150 m)
50	Weight	45 lbs./1000 ft. ² (20.2 kg/100 m ²)
	Diamond Dimension	3" LWD × 1 1/3" SWD (7.6 cm LWD × 3.3 cm SWD)
55	Resistance Lengthwise (4 ft., 122 cm wide)	.014 ohm/ft.
	Resistance Widthwise with Current Distributor	.005 ohm/ft. (0.016 ohm/m)
60	Bending Radius	3/32 inches (0.24 cm)
	Bending Radius in Mesh Plane	50 ft. (15 m).
65		

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When the coated metal mesh is used for cathodic protection, such as for retarding corrosion in steel reinforced concrete, the mesh will be connected to a current distribution member. Such a member will most always be a valve metal and preferably is the same metal alloy or intermetallic mixture as the metal most predominantly found in the expanded valve metal mesh. This current distribution member must be
5 firmly affixed to the metal mesh. One preferred manner of firmly fixing the member to the mesh is by welding, e.g., electrical resistance welding such as spot welding. Moreover, the welding can proceed through the coating. Thus, a coated current distributor strip can be laid on a coated mesh, with coated faces in contact, and yet the welding can readily proceed. The strip can be spot welded to the mesh at every node and thereby provide uniform distribution of current thereto. Such a current distributor strip member
10 positioned along a piece of mesh about every 30 meters will usually be sufficient to serve as a current distributor for such piece.

Claims

- 15 1. A coiled valve metal mesh for use, when uncoiled, as an electrode for electrochemical processes, the valve metal mesh having a pattern of substantially diamond-shaped voids having long way of design (LWD) and short way of design (SWD) dimensions for units of the pattern, the pattern of voids being defined by a continuum of valve metal strands interconnected at nodes and carrying on their surface an electrochemically active coating, wherein the mesh of valve metal is a flexible and stretchable mesh with
20 strands of thickness less than 0.125 cm and having a void fraction of at least 90%, said flexible mesh being coiled about an axis along the LWD dimension of the pattern units and being stretchable when uncoiled by up to about 10% along the SWD dimension of the pattern units and further being bendable in the general plane of the mesh about a bending radius in the range of from 5 to 25 times the width of the mesh, whereby said electrode mesh can be uncoiled onto a supporting surface on which the mesh can be stretched to an
25 operative electrode configuration.
 2. The electrode mesh of claim 1, wherein said mesh has a void fraction of about 92 to 96%.
 3. The electrode mesh of claim 1, wherein said valve metal has an elongation within the range of from 20 percent to about 40 percent.
 4. The electrode mesh of claim 1, wherein the valve metal of said mesh is selected from the group
30 consisting of titanium, tantalum, zirconium, niobium, their alloys and intermetallic mixtures.
 5. The electrode mesh of claim 4, wherein said valve metal is an annealed, unalloyed metal selected from the group consisting of titanium, tantalum, zirconium, and niobium.
 6. The electrode mesh of claim 1, wherein the mesh weight of said valve metal is within the range of from about 0.05 to about 0.5 kilogram of metal per square meter of said mesh.
 - 35 7. The electrode mesh of claim 1, wherein the mesh is expanded from a coil or sheet of solid valve metal by a factor within the range of from 15:1 to about 30:1.
 8. The electrode mesh of claim 1, wherein the mesh strands have thickness within the range of from about 0.05 centimeter to about 0.125 centimeter and width within the range of from about 0.05 centimeter to about 0.20 centimeter.
 - 40 9. The electrode mesh of claim 1, wherein said nodes have twice the strand thickness and are positioned in an at least virtually completely non-angulated vertical plane to the horizontal plane of said mesh when in uncoiled configuration.
 10. The electrode mesh of claim 1, wherein said mesh has a bending radius in the general plane of the metal within the range of from about 10 to about 20 times the width of the mesh.
 - 45 11. The electrode mesh of claim 1, which consists of an expanded mesh having a continuous network of strands connected at a multiplicity of nodes providing a redundancy of current-carrying paths through the mesh.
 12. The electrode mesh of claim 1, wherein the strands provide a pattern of voids and a continuous network of strands interconnected by between 500 and 2000 nodes per square meter of the mesh.
 - 50 13. The electrode mesh of claim 1, wherein said interconnected metal strands form substantially diamond-shaped apertures having an LWD dimension within the range of from about 4 to about 9 centimeters and an SWD dimension within the range of from about 2 to about 4 centimeters.
 14. The electrode mesh of claim 1, wherein said coil has an inner hollow zone having a diameter greater than about 20 centimeters and an outer diameter of up to 150 centimeters.
 - 55 15. The electrode mesh of claim 1, wherein the total surface area of the valve metal strands and their connections is not less than 10 percent, nor more than about 50 percent, of the area of the mesh.
 16. The electrode mesh of claim 1, wherein the electrochemically active coating contains a platinum group metal or metal oxide.
 17. The electrode mesh of claim 16, wherein said coating contains from 0.05 to 0.5 gram of catalytic
60 metal per square meter of the mesh.
 18. The electrode mesh of claim 1, wherein the electrochemically active coating contains at least one oxide selected from the group consisting of the platinum group metal oxides, magnetite, ferrite, and cobalt oxide spinel.
 19. The electrode mesh of claim 1, wherein the electrochemically active coating contains a mixed
65 crystal material of at least one oxide of a valve metal and at least one oxide of a platinum group metal.

When the coated metal mesh is used for cathodic protection, such as for retarding corrosion in steel reinforced concrete, the mesh will be connected to a current distribution member. Such a member will most always be a valve metal and preferably is the same metal alloy or intermetallic mixture as the metal most predominantly found in the expanded valve metal mesh. This current distribution member must be firmly affixed to the metal mesh. One preferred manner of firmly fixing the member to the mesh is by welding, e.g., electrical resistance welding such as spot welding. Moreover, the welding can proceed through the coating. Thus, a coated current distributor strip can be laid on a coated mesh, with coated faces in contact, and yet the welding can readily proceed. The strip can be spot welded to the mesh at every node and thereby provide uniform distribution of current thereto. Such a current distributor strip member positioned along a piece of mesh about every 30 meters will usually be sufficient to serve as a current distributor for such piece.

Claims

1. A coiled valve metal mesh for use, when uncoiled, as an electrode for electrochemical processes, the valve metal mesh having a pattern of substantially diamond-shaped voids having long way of design (LWD) and short way of design (SWD) dimensions for units of the pattern, the pattern of voids being defined by a continuum of valve metal strands interconnected at nodes and carrying on their surface an electrochemically active coating, wherein the mesh of valve metal is a flexible and stretchable mesh with strands of thickness less than 0.125 cm and having a void fraction of at least 90%, said flexible mesh being coiled about an axis along the LWD dimension of the pattern units and being stretchable when uncoiled by up to about 10% along the SWD dimension of the pattern units and further being bendable in the general plane of the mesh about a bending radius in the range of from 5 to 25 times the width of the mesh, whereby said electrode mesh can be uncoiled onto a supporting surface on which the mesh can be stretched to an operative electrode configuration.
2. The electrode mesh of claim 1, wherein said mesh has a void fraction of about 92 to 96%.
3. The electrode mesh of claim 1, wherein said valve metal has an elongation within the range of from 20 percent to about 40 percent.
4. The electrode mesh of claim 1, wherein the valve metal of said mesh is selected from the group consisting of titanium, tantalum, zirconium, niobium, their alloys and intermetallic mixtures.
5. The electrode mesh of claim 4, wherein said valve metal is an annealed, unalloyed metal selected from the group consisting of titanium, tantalum, zirconium, and niobium.
6. The electrode mesh of claim 1, wherein the mesh weight of said valve metal is within the range of from about 0.05 to about 0.5 kilogram of metal per square meter of said mesh.
7. The electrode mesh of claim 1, wherein the mesh is expanded from a coil or sheet of solid valve metal by a factor within the range of from 15:1 to about 30:1.
8. The electrode mesh of claim 1, wherein the mesh strands have thickness within the range of from about 0.05 centimeter to about 0.125 centimeter and width within the range of from about 0.05 centimeter to about 0.20 centimeter.
9. The electrode mesh of claim 1, wherein said nodes have twice the strand thickness and are positioned in an at least virtually completely non-angulated vertical plane to the horizontal plane of said mesh when in uncoiled configuration.
10. The electrode mesh of claim 1, wherein said mesh has a bending radius in the general plane of the metal within the range of from about 10 to about 20 times the width of the mesh.
11. The electrode mesh of claim 1, which consists of an expanded mesh having a continuous network of strands connected at a multiplicity of nodes providing a redundancy of current-carrying paths through the mesh.
12. The electrode mesh of claim 1, wherein the strands provide a pattern of voids and a continuous network of strands interconnected by between 500 and 2000 nodes per square meter of the mesh.
13. The electrode mesh of claim 1, wherein said interconnected metal strands form substantially diamond-shaped apertures having an LWD dimension within the range of from about 4 to about 9 centimeters and an SWD dimension within the range of from about 2 to about 4 centimeters.
14. The electrode mesh of claim 1, wherein said coil has an inner hollow zone having a diameter greater than about 20 centimeters and an outer diameter of up to 150 centimeters.
15. The electrode mesh of claim 1, wherein the total surface area of the valve metal strands and their connections is not less than 10 percent, nor more than about 50 percent, of the area of the mesh.
16. The electrode mesh of claim 1, wherein the electrochemically active coating contains a platinum group metal or metal oxide.
17. The electrode mesh of claim 16, wherein said coating contains from 0.05 to 0.5 gram of catalytic metal per square meter of the mesh.
18. The electrode mesh of claim 1, wherein the electrochemically active coating contains at least one oxide selected from the group consisting of the platinum group metal oxides, magnetite, ferrite, and cobalt oxide spinel.
19. The electrode mesh of claim 1, wherein the electrochemically active coating contains a mixed crystal material of at least one oxide of a valve metal and at least one oxide of a platinum group metal.



20. The electrode mesh of claim 1, wherein the valve metal is titanium and the electrochemically active coating is a mixed crystal material consisting essentially of titanium oxide and ruthenium oxide.

21. Use of the mesh of any of the preceding claims, in uncoiled configuration on a supporting surface, as an electrode.

22. Use of the mesh in accordance with claim 21, in which the electrode further comprises a valve metal current distributor member metallurgically bonded to strands of said mesh for distributing current to said mesh.

23. Use of the mesh in accordance with claim 22, wherein the current distributor member is coated with an electrochemically active coating and the coated member is electrically resistance welded to the coated mesh on facing coating surfaces.

24. Use of mesh in accordance with claim 21, 22 or 23 as an anode in the cathodic protection of reinforcing steel in concrete.

25. A method of manufacturing a coiled valve metal mesh for use, when uncoiled, as an electrode for electrochemical processes of the type comprising a valve metal mesh provided with a pattern of substantially diamond shaped voids having long way of design (LWD) and short way of design (SWD) dimensions for units of the pattern, the pattern of voids being defined by a continuum of thin valve metal strands interconnected at nodes and carrying on their surface an electrocatalytic coating, comprising:

(a) providing a flexible, coiled valve metal mesh of thickness less than 0.125cm having a void fraction of at least 90 percent, said mesh being elongated along the direction of the SWD dimension of the pattern and being coiled about an axis along the direction of the LWD dimension of the pattern, and

(b) applying an electrocatalytic coating to the surface of the valve metal mesh while same is coiled to provide a flexible coated mesh electrode in coiled configuration, the mesh being uncoilable from the coiled configuration for use as an electrode.

26. The method of claim 25, wherein said coiled mesh is contacted with liquid coating composition providing an electrocatalytic coating having a coating weight of less than about 0.5 gram of platinum group metal per square meter of the metal mesh substrate.

27. The method of claim 25, wherein said coating is applied by dipping the mesh into coating composition and rotating the mesh while dipped into said composition.

28. The method of claim 25, wherein said coiled mesh is coiled from expanded metal mesh obtained by expanding a sheet or coil of solid metal by an expansion factor of at least 15:1 and to an at least 90 percent void fraction.

29. The method of claim 25, wherein the valve metal mesh has a weight of not above about 0.5 kilogram per square meter.

30. The method of claim 25, which further comprises the step of installing the mesh as an electrode by uncoiling the metal mesh from the coiled configuration and welding a valve metal current distributor member to the uncoiled metal mesh electrode.

31. The method of claim 29, wherein the valve metal current distributor member carries an electrocatalytic coating on its surface, and at least one coated surface of the distributor member is welded to the coated surface of the valve metal mesh at points of connection of the valve metal mesh electrode stands.

Patentansprüche

1. Aufgewickeltes Ventilmetalldrahtnetz, das in abgewickeltem Zustand als Elektrode für elektrochemische Verfahren dient, wobei das Ventilmetalldrahtnetz ein Muster von im wesentlichen rautenförmigen Öffnungen mit einer langen (LWD) und einer kurzen (SWD) Abmessung für Einheiten des Musters aufweist, das Öffnungsmuster durch ein Kontinuum von Ventilmetalldrängen definiert ist, die an Knotenpunkten miteinander verbunden sind und auf ihrer Oberfläche einen elektrochemisch aktiven Überzug tragen, das Netz aus Ventilmetalldraht ein flexibles und streckbares Drahtnetz mit Strängen einer Dicke von weniger als 0,125 mm ist und einen Öffnungsanteil von mindestens 90% aufweist, und das flexible Netz um eine entlang der LWD-Abmessung der Mustereinheiten verlaufende Achse aufgewickelt ist und um bis zu etwa 10% entlang der SWD-Abmessung der Mustereinheiten streckbar ist, wenn es abgewickelt ist, und außerdem in der Hauptebene des Netzes zu einem Biegeradius im Bereich von 5 bis 25 mal der Maschenbreite biegsam ist, wodurch das Elektrodennetz auf eine Trägerfläche abgewickelt werden kann, auf der das Netz zu einer Betriebselektrodenkonfiguration gestreckt werden kann.

2. Elektrodennetz nach Anspruch 1, bei dem das Netz einen Lückenanteil von etwa 92 bis 96% aufweist.

3. Elektrodennetz nach Anspruch 1, bei dem das Ventilmetalldraht eine Streckbarkeit im Bereich von 20% bis etwa 40% aufweist.

4. Elektrodennetz nach Anspruch 1, bei dem das Ventilmetalldraht des Netzes aus der Gruppe von Titan, Tantal, Zirkonium, Niob, deren Legierungen und intermetallischen Mischungen ausgewählt ist.

5. Elektrodennetz nach Anspruch 4, bei dem das Ventilmetalldraht ein geglühtes, unlegiertes Metall ausgewählt aus der Gruppe von Titan, Tantal, Zirkonium und Niob ist.

6. Elektrodennetz nach Anspruch 1, bei dem das Gewicht des Ventilmetalldrahtnetzes im Bereich von etwa 0,05 bis etwa 0,5 kg Metall pro Quadratmeter des Netzes liegt.



7. Elektrodenetz nach Anspruch 1, bei dem das Netz ausgehend von einer Rolle oder einem Blech aus festem Ventilmaterial um einen Faktor im Bereich von 15:1 bis etwa 30:1 ausgedehnt ist.
8. Elektrodenetz nach Anspruch 1, bei dem die Netzstränge eine Dicke im Bereich von etwa 0,05 cm bis etwa 0,125 cm und eine Breite im Bereich von etwa 0,05 cm bis etwa 0,20 cm aufweisen.
9. Elektrodenetz nach Anspruch 1, bei dem die Knotenpunkte die zweifache Strangdicke haben und in einer zumindest praktisch vollständig ungewinkelten vertikalen Ebene bezogen auf die horizontale Ebene des Netzes angeordnet sind, wenn dieses abgewickelt ist.
10. Elektrodenetz nach Anspruch 1, bei dem das Netz einen Biegeradius in der Hauptebene des Metalles im Bereich von etwa 10- bis etwa 20-mal der Maschenbreite aufweist.
11. Elektrodenetz nach Anspruch 1, das aus einem ausgedehnten Netz mit einem kontinuierlichen Netzwerk von Strängen besteht, die an einer Vielzahl von Knotenpunkten verbunden sind, wodurch eine Redundanz der stromleitenden Wege über das Netz geschaffen wird.
12. Elektrodenetz nach Anspruch 1, in dem die Stränge ein Muster von Öffnungen und ein kontinuierliches Netzwerk von durch zwischen 500 und 2000 Knotenpunkten pro Quadratmeter des Netzes miteinander verbundenen Strängen schaffen.
13. Elektrodenetz nach Anspruch 1, in dem die miteinander verbundenen Metallstränge im wesentlichen rautenförmige Öffnungen mit einer LWD-Abmessung im Bereich von etwa 4 bis etwa 9 cm und einer SWD-Abmessung im Bereich von etwa 2 bis etwa 4 cm bilden.
14. Elektrodenetz nach Anspruch 1, bei dem die Rolle einen inneren hohlen Bereich mit einem Durchmesser von mehr als etwa 20 cm und einen äußeren Durchmesser von bis zu 150 cm aufweist.
15. Elektrodenetz nach Anspruch 1, bei dem die Gesamtoberfläche der Ventilmaterialstränge und ihrer Verbindungen nicht weniger als 10% und nicht mehr als etwa 50% der Fläche des Netzes beträgt.
16. Elektrodenetz nach Anspruch 1, bei dem der elektrochemisch aktive Überzug ein Platingruppenmetall oder -metalloxid enthält.
17. Elektrodenetz nach Anspruch 16, bei dem der Überzug 0,05 bis 0,5 g katalytisches Metall pro Quadratmeter des Netzes enthält.
18. Elektrodenetz nach Anspruch 1, bei dem der elektrochemisch aktive Überzug mindestens ein Oxid ausgewählt aus der Gruppe von Platingruppenmetalloxiden, Magnetit, Ferrit und Kobaltoxid-Spinell enthält.
19. Elektrodenetz nach Anspruch 1, bei dem der elektrochemisch aktive Überzug ein Mischkristallmaterial von mindestens einem Oxid eines Ventilmaterials und mindestens einem Oxid eines Platingruppenmetalles enthält.
20. Elektrodenetz nach Anspruch 1, bei dem das Ventilmaterial Titan ist und der elektrochemisch aktive Überzug ein Mischkristallmaterial ist, welches im wesentlichen aus Titanoxid und Rutheniumoxid besteht.
21. Verwendung des Netzes nach einem der vorangehenden Ansprüche in abgewickelter Form auf einer Trägerfläche als Elektrode.
22. Verwendung des Netzes nach Anspruch 21, wobei die Elektrode außerdem ein metallurgisch an die Stränge des Netzes gebundenes Ventilmaterial-Stromverteilerelement zur Verteilung von Strom an das Netz aufweist.
23. Verwendung des Netzes nach Anspruch 22, wobei das Stromverteilerelement mit einem elektrochemisch aktiven Überzug überzogen ist und das überzogene Element mit dem überzogenen Netz an gegenüberliegenden Überzugsflächen durch elektrische Widerstandsschweißung verbunden ist.
24. Verwendung des Netzes nach Anspruch 21, 22 oder 23 als Anode beim kathodischen Schutz von verstärktem Stahl in Beton.
25. Verfahren zur Herstellung eines aufgewickelten Ventilmaterialdrahtnetzes zur Verwendung, wenn dieses abgewickelt ist, als Elektrode für elektrochemische Verfahren, wobei das Netz von einem Typ ist, der ein Ventilmaterialnetz aufweist, welches mit einem Muster aus im wesentlichen rautenförmigen Öffnungen mit einer langen (LWD) und einer kurzen (SWD) Abmessung für Einheiten des Musters ausgestattet ist, und das Muster der Öffnungen durch ein Kontinuum von dünnen Ventilmaterialsträngen definiert ist, die an Knotenpunkten miteinander verbunden sind und auf ihrer Oberfläche einen elektrokatalytischen Überzug tragen, wobei man bei dem Verfahren
- a) ein flexibles, aufgewickelter Ventilmaterialnetz einer Dicke von weniger als 0,125 cm mit einem Öffnungsanteil von mindestens 90% zur Verfügung stellt, wobei das Netz entlang der Richtung der SWD-Abmessung des Musters gedehnt und um eine Achse entlang der Richtung der LWD-Abmessung des Musters aufgewickelt ist, und
 - b) einen elektrokatalytischen Überzug auf das Ventilmaterialnetz aufbringt, während dieses aufgewickelt ist, um eine flexible überzogene Netzelektrode in aufgewickelter Anordnung zu schaffen, wobei das Netz aus der aufgewickelten Anordnung zur Verwendung als Elektrode abgewickelt werden kann.
26. Verfahren nach Anspruch 25, bei dem das aufgewickelte Netz mit flüssiger Überzugszusammensetzung kontaktiert wird, die einen elektrokatalytischen Überzug mit einem Überzugsgewicht von weniger als etwa 0,5 g Platingruppenmetall pro Quadratmeter des Metallnetzsubstrates zur Verfügung stellt.
27. Verfahren nach Anspruch 25, bei dem der Überzug durch Eintauchen des Netzes in Überzugszusammensetzung und Rotieren des Netzes aufgebracht wird, während dieses in die Zusammensetzung eintaucht.



28. Verfahren nach Anspruch 25, bei dem das aufgewickelte Netz durch Aufwickeln von ausgedehntem Metallnetz hergestellt wird, welches erhalten wird, indem ein Blech oder eine Rolle des festen Metalles um einen Ausdehnungsfaktor von mindestens 15:1 und auf einen Öffnungsanteil von mindestens 90% ausgedehnt wird.

5 29. Verfahren nach Anspruch 25, bei dem das Ventilmetalldrahtnetz ein Gewicht von nicht mehr als etwa 0,5 kg pro Quadratmeter aufweist.

30. Verfahren nach Anspruch 25, bei dem außerdem das Netz als Elektrode montiert wird, indem das Metallnetz aus der aufgewickelten Anordnung abgewickelt und ein Ventilmetal-Stromverteilerelement an die abgewickelte Metallnetzelektrode geschweißt wird.

10 31. Verfahren nach Anspruch 29, bei dem das Ventilmetal-Stromverteilerelement auf seiner Oberfläche einen elektrokatalytischen Überzug trägt und mindestens eine überzogene Fläche des Verteilerelementes an der überzogenen Fläche des Ventilmetalnetzes an Verbindungspunkten der Ventilmetalnetz-Elektrodenstränge angeschweißt wird.

15 Revendications

1. Une maille en métal d'arrêt enroulée destinée à être utilisée, lorsqu'elle est déroulée, comme électrode pour des procédés électrochimiques, la maille en métal d'arrêt ayant un motif de vides substantiellement en forme de diamant ayant une longueur dite LWD et une largeur dite SWD pour les
20 unités de motif, le motif des vides étant défini par un continuum de rubans en métal d'arrêt interconnectés à des nœuds et portant sur leur surface un revêtement électrochimiquement actif, la maille en métal d'arrêt étant une maille flexible et étirable avec des rubans d'une épaisseur inférieure à 0,125 cm et ayant une fraction vide d'au moins 90%, ladite maille flexible étant enroulée autour d'un axe selon la dimension LWD des unités de motif et étant étirable lorsque déroulée jusqu'à environ 10% le long de la dimension SWD des
25 unités de motif et étant de plus pliable dans le plan général de la maille selon un rayon de pliage dans l'intervalle de 5 à 25 fois la largeur de la maille, de sorte que ladite maille d'électrode peut être déroulée sur une surface de support sur laquelle la maille peut être étirée dans une configuration d'électrode opérante.

2. La maille d'électrode de la revendication 1, dans laquelle ladite maille a une fraction vide de 92 à 96 %.

30 3. La maille d'électrode de la revendication 1, dans laquelle ledit métal d'arrêt a une élongation dans l'intervalle de 20 pourcent à environ 40 pourcent.

4. La maille d'électrode de la revendication 1, dans laquelle ledit métal d'arrêt de ladite maille est sélectionné dans le groupe constitué du titane, tantale, zirconium, niobium, leurs alliages et mélanges intermétalliques.

35 5. La maille d'électrode de la revendication 4, dans laquelle ledit métal d'arrêt est un métal recuit, pur sélectionné dans le groupe constitué du titane, du tantale, du zirconium et du niobium.

6. La maille d'électrode de la revendication 1, dans laquelle ledit métal d'arrêt est dans l'intervalle d'environ 0,05 à environ 0,5 kilogramme de métal par mètre carré de ladite maille.

40 7. La maille d'électrode de la revendication 1, dans laquelle la maille est obtenue par l'expansion d'un rouleau ou d'une feuille de métal d'arrêt solide par un facteur dans l'intervalle d'environ 15:1 à environ 30:1.

8. La maille d'électrode de la revendication 1, dans laquelle les rubans de maille ont une épaisseur dans l'intervalle d'environ 0,05 centimètre à environ 0,125 centimètre et une largeur dans l'intervalle d'environ 0,05 centimètre à environ 0,20 centimètre.

45 9. La maille d'électrode de la revendication 1, dans laquelle lesdits nœuds ont le double de l'épaisseur du ruban et sont positionnés dans un plan vertical au moins virtuellement non-angulé au plan horizontal de ladite maille lorsqu'elle est en configuration déroulée.

10. La maille d'électrode de la revendication 1, dans laquelle ladite maille a un rayon de pliage dans le plan général du métal dans l'intervalle d'environ 10 à environ 20 fois la largeur de la maille.

50 11. La maille d'électrode de la revendication 1, qui consiste en une maille expansée ayant un réseau continu de rubans connectés à une multiplicité de nœuds établissant une redondance de chemins conducteurs de courant à travers la maille.

12. La maille d'électrode de la revendication 1, dans laquelle les rubans constituent un motif de vides et un réseau continu de rubans interconnectés par entre 500 et 2000 nœuds par mètre carré de maille.

55 13. La maille d'électrode de la revendication 1, dans laquelle lesdits rubans de métal interconnectés forment des ouvertures substantiellement en forme de diamant ayant une dimension LWD dans l'intervalle d'environ 4 à environ 9 centimètres et une dimension SWD dans l'intervalle d'environ 2 à environ 4 centimètres.

60 14. La maille d'électrode de la revendication 1, dans laquelle ledit rouleau a une zone intérieure creuse ayant un diamètre supérieur à 20 centimètres et jusqu'à 150 centimètres.

15. La maille d'électrode de la revendication 1, dans laquelle la surface totale des rubans de métal d'arrêt et leur connections n'est pas inférieure à 10 pourcent, ni supérieure à 50 pourcent, de la surface de la maille.

65 16. La maille d'électrode de la revendication 1, dans laquelle le revêtement électrochimiquement actif contient un métal ou un oxyde de métal du groupe du platine.



17. La maille d'électrode de la revendication 16, dans laquelle ledit revêtement contient de 0,05 à 0,5 gramme de métal catalytique par mètre carré de maille.

18. La maille d'électrode de la revendication 1, dans laquelle le revêtement électrochimiquement actif contient au moins un oxyde sélectionné du groupe composé des oxydes de métaux du groupe du platine, de la magnétite, de la ferrite, et de spinelle d'oxyde de cobalt.

19. La maille d'électrode de la revendication 1, dans laquelle le revêtement électrochimiquement actif contient un matériau à cristaux mixtes d'au moins un oxyde d'un métal d'arrêt et au moins un oxyde d'un métal du groupe du platine.

20. La maille d'électrode de la revendication 1, dans laquelle le métal d'arrêt est le titane et le revêtement électrochimiquement actif est un matériau à cristaux mixtes constitué essentiellement d'oxyde de titane et d'oxyde de ruthénium.

21. L'utilisation de la maille de n'importe quelle des revendications précédentes, en configuration déroulée sur une surface de support, comme électrode.

22. L'utilisation de la maille en accord avec la revendication 21, dans laquelle l'électrode comprend de plus un membre distributeur de courant en métal d'arrêt lié métallurgiquement aux rubans de ladite maille pour la distribution de courant à ladite maille.

23. L'utilisation de la maille en accord avec la revendication 22, dans laquelle le membre distributeur de courant est revêtu avec un revêtement électrochimiquement actif et le membre revêtu est soudé par résistance électrique à la maille revêtue par des surfaces revêtues en face.

24. L'utilisation de la maille en accord avec la revendication 21, 22 ou 23, comme anode dans la protection cathodique d'acier de renforcement dans du béton.

25. Une méthode de fabrication d'une maille enroulée en métal d'arrêt destinée à être utilisée, lorsqu'elle est déroulée, comme électrode pour des procédés électrochimiques, du type comprenant une maille en métal d'arrêt pourvu d'un motif de vides substantiellement en forme de diamant ayant une longueur dite LWD et une largeur dite SWD pour les unités de motif, le motif des vides étant défini par un continuum de fins rubans en métal d'arrêt interconnectés à des nœuds et portant sur leur surface un revêtement électrochimiquement actif, comprenant les étapes:

(a) de fournir une maille en métal d'arrêt flexible, enroulée d'une épaisseur inférieure à 0,125 cm et ayant une fraction de vide d'au moins 90%, ladite maille étant enroulée autour d'un axe selon la direction de la dimension LWD du motif, et

(b) d'appliquer un revêtement électrocatalytique à la surface de la maille en métal d'arrêt alors que celle-ci est enroulée pour constituer une électrode à maille revêtue flexible en configuration enroulée, la maille étant déroulable de la configuration enroulée pour l'utilisation comme électrode.

26. La méthode de la revendication 25, dans laquelle ladite maille enroulée est mise en contact avec une composition de revêtement liquide fournissant un revêtement électrocatalytique ayant un poids de revêtement de moins d'environ 0,5 gramme de métal du groupe du platine par mètre carré de substrat de maille en métal.

27. La méthode de la revendication 25, dans laquelle le revêtement est appliqué en trempant la maille dans la composition de revêtement et en tournant la maille pendant qu'elle est trempée dans ladite composition.

28. La méthode de la revendication 25, dans laquelle ladite maille est enroulée d'une maille expansée obtenu par l'expansion d'une feuille ou d'un rouleau de métal solide par un facteur d'expansion d'au moins 15:1 et à une fraction vide d'au moins 90%.

29. La méthode de la revendication 25, dans laquelle la maille en métal d'arrêt a un poids qui n'est pas supérieur à environ 0,5 kilogramme par mètre carré.

30. La méthode de la revendication 25, qui comprend de plus une étape d'installation de la maille comme électrode en déroulant la maille de métal de la configuration enroulée et en soudant un membre distributeur de courant en métal d'arrêt à l'électrode en maille de métal déroulée.

31. La méthode de la revendication 29, dans laquelle le membre distributeur de courant en métal d'arrêt porte à sa surface un revêtement électrocatalytique, et au moins une surface revêtue du membre distributeur de courant est soudée à la surface revêtue de la maille en métal d'arrêt à des points de connexion de cordons de la maille d'électrode en métal d'arrêt.

