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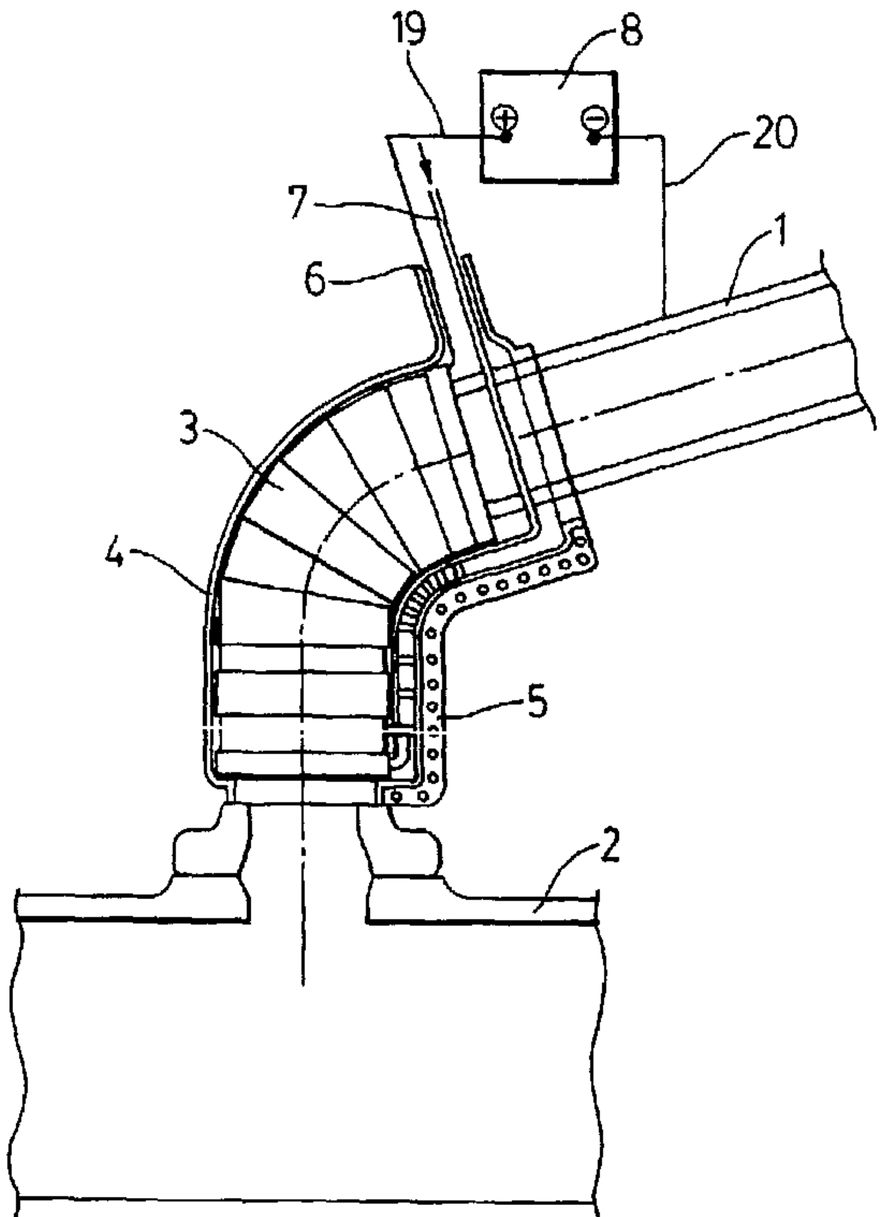
(71) Demandeur/Applicant:
INTEGRAN TECHNOLOGIES INC., CA

(72) Inventeurs/Inventors:
PALUMBO, GINO, CA;
BROOKS, IAIN, CA;
ROBERTSON, ANDREW J., CA;
PANAGIOTOPOULOS, KONSTANTINOS, CA;
GONZALES, FRANCISCO, CA;
TOMANTSCHGER, KLAUS, CA

(74) Agent: RIDOUT & MAYBEE LLP

(54) Titre : PROCEDE DESTINE A L'ELECTROFORMAGE IN SITU D'UNE COUCHE STRUCTURELLE EN MATERIAU METALLIQUE SUR UNE PAROI EXTERIEURE D'UN TUBE METALLIQUE

(54) Title: PROCESS FOR IN-SITU ELECTROFORMING A STRUCTURAL LAYER OF METALLIC MATERIAL TO AN OUTSIDE WALL OF A METAL TUBE



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A process for in situ electroforming a structural reinforcing layer of selected metallic material for repairing an external surface area of a degraded section of metallic workpieces, especially of tubes and tube sections, is described. Preferably, the metal layer coatings are made of fine-grained metals, metal alloys or metal matrix composites. The plating system can be used on straight tubes, tube joints to different diameter tubes or face plates, tube elbows and other complex shapes encountered in piping systems. A suitable apparatus is assembled on or near the degraded site and is sealed in place to form the plating cell. Also described is a process for plating "patches" onto degraded areas by selective plating including brush plating.

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(71) Applicant: **INTEGRAN TECHNOLOGIES INC.** [CA/CA]; 1 Meridian Road, Toronto, Ontario M9W 4Z6 (CA).

(72) Inventors: **PALUMBO, Gino**; 9 Tyler Place, Toronto, Ontario M9R 1L8 (CA). **BROOKS, Iain**; 33 Glebe Road E., Apt. 3, Toronto, Ontario M4S 1N7 (CA). **ROBERTSON, J.**; 10 Eltham Drive, Toronto, Ontario M8W 2H9 (CA). **PANAGIOTOPOULOS, Konstantinos**; 9 Tyler Place, Toronto, Ontario M9R 1L8 (CA). **GONZALEZ, Francisco**; 18 Larkin Avenue, Toronto, Ontario M6S 1L8 (CA). **TOMANTSCHGER, Klaus**; 6197 Montevideo Road, Mississauga, Ontario L5N 2E8 (CA).

(74) Agent: **MITCHELL, Randall**; Ridout & Maybee LLP, One Queen St. East, Suite 2400, Toronto, Ontario M5C 3B1 (CA).

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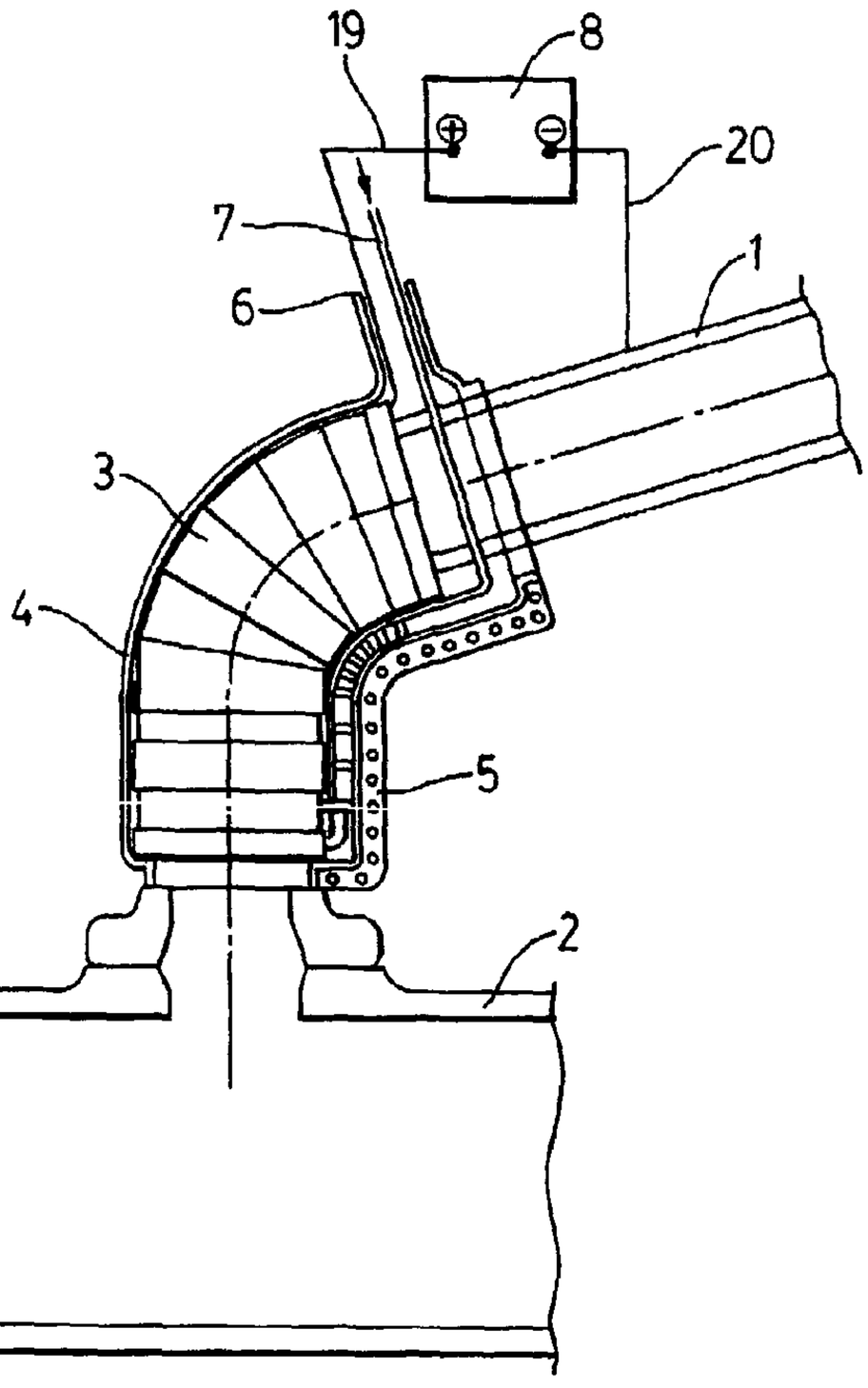
(54) Title: PROCESS FOR IN-SITU ELECTROFORMING A STRUCTURAL LAYER OF METALLIC MATERIAL TO AN OUTSIDE WALL OF A METAL TUBE



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PROCESS FOR IN-SITU ELECTROFORMING A STRUCTURAL LAYER OF METALLIC MATERIAL TO AN OUTSIDE WALL OF A METAL TUBE

BACKGROUND OF THE INVENTION

1. Technical Field

This invention relates to a process and apparatus for electroplating a metal patch on the outside or exterior surface of a damaged or degraded portion of a metallic workpiece, especially a degraded or damaged portion of a metallic pipe or conduit. In particular a degraded or damaged (hereinafter referred to as degraded) portion of a metallic pipe or conduit (hereinafter referred to as a pipe) may be repaired in accordance with this invention without having to remove the pipe from an apparatus or installation in which the pipe is connected for the conveyance of fluids (i.e., *in situ* repair of the pipe). The method and apparatus is particularly suitable for the *in situ* repair and maintenance of feeder pipe systems in nuclear reactors and applications where degradation of the pipes occur by localized and general corrosion, stress corrosion cracking, fatigue, erosion and the like. Formation of the *in situ* patch uses an apparatus which is configured to form a water tight electrolytic plating cell around the degraded portion of the pipe. The plating cell which is advantageously confined to the degraded portion of the pipe, is used to form a patch of fine grained electrolytically deposited metal or metal alloy, which optionally includes particulate material entrapped therein, wherein the electroplated metal or metal allow has an average grain size of 10-1000 nm,

and desirably contains a portion of nanocrystalline grain size electrodeposited metal or metal alloy. The electrodeposition employs pulse electrodeposition with a total duty cycle of 10-100%.

2. Background Art

Tubes and pipes are commonly used e.g. in heat exchangers in various applications in the chemical and nuclear industry, in above-ground and underground pipelines for the transport of fluids including liquid petroleum fuel, water, sewer, natural gas, etc. In a variety of these applications the tube material locally degrades with time and means are sought to repair a damaged section by a convenient and cost-effective method.

A number of sleeving methods that involve welding, re-lining with appropriate sleeves, as well as electroforming sleeves for application to the inside of degraded pipe sections have been disclosed in the prior art.

Malagola in US 4,624,750 (1986) describes a process for corrosion protection of a steam generator tube before final assembly wherein a metallic layer is deposited on the inside of the tube. This invention is specifically directed to applying a protective coating to the inside of tubes. In one embodiment, however, the outer surface of the tube, is also electroplated with a 0.1mm layer of electrolytic Ni before it is installed in the tube plate. The process relies on plating a thin corrosion resistant protective layer and is neither intended nor suitable for the outside repair of degraded tube sections already in service.

Erb in US 5,352,266 (1994), and US 5,433,797 (1995) describes a process for producing nanocrystalline materials, particularly nanocrystalline nickel. The nanocrystalline material is electrodeposited onto the cathode in an aqueous acidic electrolytic cell by application of a pulsed DC current. The cell

also optionally contains stress relievers. Products of the invention include wear resistant coatings, magnetic materials and catalysts for hydrogen evolution.

Palumbo in U.S. 5,527,445 (1996), U.S. 5,516,415 (1996) and in US 5,538,615 (1996) discloses a plating process for the repair of nuclear steam generator tubes by in-situ electroforming a structural layer on the inside of the degraded tube section. The electrosleeve is applied by a convenient remote process for forming a structural layer on the inside of the affected tube section. The inner diameter of the tube to be repaired is at least 5mm, but typically between 1cm and 5cm. The thickness of the electroformed layer is typically 0.1 to 2mm and its length ranges from 10cm to 90cm.

Michaut in U.S. 5,660,705 (1997) describes a thick, non-magnetic Ni-B metal plating sleeve on the inside of a tube to repair a steam generator tube crimped in a tube plate. The inside diameter of the tube to be repaired is 2cm and the coating thickness ranges from 0.5 to 1.5mm.

Although quite elegant, the electrosleeve process applied to inside tube surfaces of nuclear steam generator tubes does have limitations. Namely the thickness of the coating is limited typically to less than 1mm due to considerations such as probe removal, flow restriction, coating surface finishing and need for maintaining a non-destructive inspection capability such as eddy current or ultrasound testing. Thin coatings inside the tube are frequently insufficient to reestablish the original mechanical properties. Relying on a substantial grain size reduction to enable a complete structural repair compromises other physical properties such as ductility. The method of handling and sealing the probe against the inside tube wall can, at times, be challenging. The process is neither well suited for small inner diameter tubes (<0.5cm) nor larger ones (>5cm). Probe insertion/removal may be difficult due to the location of the damaged area and the geometry of the tubing, e.g. in long and more complex piping systems involving elbows, tees, various inner

diameter piping etc. In some of these circumstances the damaged areas to be repaired are more easily accessible from the outside of the tube. The application of a suitable sleeve in regions other than straight areas, such as bends, elbows, tees and the like can be difficult as well. Inside diameter electrodeposition repairs provide a sleeve of essentially uniform thickness which may not be desired/required, e.g. in the case of larger inner diameter tubes with very localized damaged areas, a "patch" may be a more suitable repair technique as compared to sleeving the entire tube section, thereby minimizing build up of additional material and minimizing heat exchange property changes. Alternatively, an outside outer diameter repair can be carried out without disrupting the power plant operation. Therefore the need exists for a repair technique that can be used in applications not currently satisfied by inside inner diameter electrodeposition methods noted above.

SUMMARY OF THE INVENTION

It is an objective of the invention to repair corroded, eroded, cracked or other degraded sections of a metallic workpiece including e.g. at least a section of a tube, optionally with more complex geometries such as elbows, tees, flanges and connections to e.g. base plates and the like by applying a suitable metallic coating to the outer surface of the damaged section using electrodeposition. It is a further objective of this invention to provide a process for plating a fine-grained metal, metal alloy or metal matrix composite on the external surface of a tube section to institute a full structural repair.

It is a further objective of this invention to provide an apparatus for the *in situ* electrodeposition of a structural reinforcing layer of selected metallic material on an external surface of a degraded section of a metallic workpiece, especially a pipe.

These and other objectives are obtained by the below described process and apparatus for *in situ* electrodepositing a structural reinforcing layer of selected metallic material on an external surface of a degraded section of a metallic workpiece such as a pipe. When a degraded section of pipe or tubing is repaired in accordance with this invention, the wall of the pipe is restored to its original mechanical design specifications, including burst pressure, bend strength, fatigue and corrosion performance.

The process of the invention may be applied to establish a thick corrosion resistant coating of a metal (e.g., pure metal except for incidental impurities) selected from the group consisting of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Pt, Rh, Ru, Sn, Mo, Mn, W, V, and Zn. Alternatively, the invention may be used to establish a thick corrosion resistant coating of a metal alloy wherein the metal alloy contains a combination of two or more of the aforementioned metals. In addition, the metal alloy may further comprise an alloying element selected from the group consisting of B, C, P, S and Si. The metal alloy may also comprise one of the above listed metals alloyed with at least one of the aforementioned alloying elements. Furthermore, the aforementioned metal or metal alloys may further comprise particulate additives which become entrapped in the metal during the electroplating procedure. Suitable particulate additives include particulates selected from the group consisting of metal powder, metal alloy powder, metal oxide powder, nitride powder, carbon (either graphite or diamond), carbide powder, MoS_2, and organic material such as polymer spheres and particulate PTFE. Suitable metal oxide powders include metal oxide of Al, Co, Cu, In, Mg, Ni, Si, Sn, V, and Zn. Suitable nitrides include the nitrides of Al, B, C and Si. Suitable carbides include the carbides of B, Cr, Bi, Si and W.

The process may be employed to create high strength equiaxed coatings on the outside of degraded tubes in nuclear reactors, industrial plants, above ground and underground pipelines, pipe systems and related applications. The

process is particularly advantageous since the degraded portion of the metallic workpiece may be repaired by electroplating a metal patch on the outside of the degraded portion of the pipe without having to remove the pipe from the apparatus or installation in which the pipe is used to convey fluids. In other words the process provides an *in situ* repair of the pipe. The invention may also be practiced on a non in situ workpiece such as a pipe which is not connected to an apparatus or installation.

The process may be carried out by providing a plating cell around the degraded portion of the pipe, preferably without removing the pipe from the environment or installation in which it is utilized. The plating cell includes a housing which is configured so that it may be clamped around the pipe to provide a fluid tight or leak tight volume between the pipe and the housing for the circulation of electrolyte or plating solution through the volume within the plating cell. An anode is provided within the housing. The anode is preferably located in the vicinity of the degraded portion of the pipe within the housing. More than one anode may be utilized. Preferably the anode or anodes surround the degraded portion of the pipe and extend lengthwise beyond the degraded portion of the pipe so that the electroplated metal formed by the electroplating process forms a patch which extends slightly beyond the degraded portion of the pipe. The plating cell also includes appropriate electrical wiring and electrical connections for connection to a source of electric current required for the electroplating procedure. A wire is connected to the pipe undergoing repair so that the pipe functions as a cathode. Thus the cell includes at least one anode and a cathode with electrical connections to a source of electric current. The housing of the plating cell further includes a fluid supply inlet and a fluid supply outlet so that the electrolyte or plating solution which contains ions of the metal to be plated, can be circulated through the housing of the plating cell. In addition the electrolyte or plating solution is desirably maintained at an ideal electroplating temperature (e.g., 0°C to 85°C) by cooling or heating. For example the fluid supply inlet and outlet may be

connected to a temperature controlled reservoir for the regulation of the temperature of the plating solution or other fluid which is circulated through the plating cell. The supply inlet and outlet may also be connected to a source of other fluids used in the process. For example, the inlets and outlets may be connected to a source of cleaning fluid such as surface cleaning fluid, activation fluid, striking fluid and electrochemical polishing fluid. Appropriate valves which are well known to those skilled in the art may be utilized to select a particular fluid which is to be circulated through the plating cell. For example a cleaning fluid may be first circulated through the plating cell to clean the exterior of the pipe prior to the circulation of the plating solution.

In operation the housing is positioned and closed to provide a leak tight seal around the surface of the workpiece to be plated. The fluid supply inlets and outlets are connected to a temperature controlled reservoir in order to enable the circulation of fluids to and from the workpiece to be plated. Other methods for controlling the temperature of a circulating fluid may be used instead of a temperature controlled reservoir. For example, the fluid supplied to the inlet may be passed through a cooling or heating device such as a heat exchanger, which is regulated to supply the fluid at the desired temperature.

Electrical connections are provided to the workpiece to be plated and to one or several anodes used in the apparatus to thereby form the in-situ plating cell around the workpiece area to be plated. Electric current is supplied to the cathode and anode while the plating solution is circulated through the plating cell to thereby electroform a structural layer of metallic material. The plating conditions are selected so that the plated material on the external surface of the degraded section of the metallic workpiece has an average grain size which is equal to or less than 1000 nm. The electrodeposition takes place using DC or pulse electrodeposition at a deposition rate of at least 0.05 mm per hour (0.05 mm/h) while the aqueous electrolyte or plating solution which contains ions of the metal to be plated, is circulated through the plating cell. This is

accomplished by passing single or multiple D.C. cathodic-current pulses between the anode and the workpiece area to be plated (i.e., the cathode) at a cathodic-current pulse frequency in the range of about 0 to 1000 Hz at pulsed intervals during which the current passes for a t_{on}-time period of at least 0.1 msec and does not pass for a t_{off}-time period in the range of about 0 to 500 msec, and passing single or multiple D.C. anodic-current pulses between the cathode and the anode at intervals during which the current passes for a t_{anodic}-time period in the range of 0 to 50 msec, the total duty cycle being in the range of 10 to 100%.

According to another aspect of this invention the in situ repair of the pipe may be carried out without enclosing the area of the article to be coated and forming a plating bath around it. In particular, brush or tampon plating is a suitable alternative, particularly when only a small portion of the workpiece is to be plated. The brush plating apparatus typically employs a soluble or dimensionally stable anode wrapped in an absorbent separator felt to form an anode brush. The brush is rubbed against the surface to be plated in a manual or mechanized mode and electrolyte solution containing ions of the metal or metal alloys to be plated is injected into the separator felt.

The present invention provides suitable coatings which function as a patch over the degraded portion of the workpiece by an electroplating procedure without the need to remove the article from the installation and without the need to submerse the entire article to be repaired into a plating bath. Thus, a portion of the workpiece such as a pipe is not covered by the reinforcing metallic patch. In other words the reinforcing metallic patch is formed on an exterior surface of the workpiece wherein the patch covers the degraded portion of the workpiece without covering at least a portion of a non-degraded portion of the workpiece. Thus the patch is substantially confined to the degraded portion of the workpiece although there may be some overlap onto non-degraded portions of the workpiece, but it is not essential to cover the

entire workpiece with the patch. By a "non-degraded portion of the workpiece" it is meant that this portion of the workpiece has not been degraded to the point of needing repair which means that the non-degraded portion of the workpiece can function as intended.

In the process of the present invention both DC and pulse-plating processes may be utilized. Pulse-plating processes may consist of a single cathodic on-time or multiple cathodic on-times of different current densities and single or multiple off-times per cycle.

A significant feature of the invention relates to the grain size of the metal or metal alloy which is electrodeposited to form the patch. All of the grain sizes mentioned herein are average grain sizes unless specifically indicated otherwise. The electroformed metal coatings of this invention have an average grain size equal to or less than 1 micron (1000 nm), preferably in the range of 10 to 750 nm, more preferably between 30 and 500 nm and even more preferably between 50 and 300 nm. In instances where ductility is not critical, the average grain size may be 100 nm or less. A metal which has an average grain size which is less than or equal to 100 nanometers is considered as having a nanocrystalline structure. Ductility of the metal is diminished as the grain size becomes smaller. Accordingly, it is generally not ideal to electrodeposit the metal with an average grain size below 10 nm because the ductility would be very low. The reduced grain size of the electrodeposited metals produced in accordance with this invention have high strength and they therefore produce a strong patch with a minimum of thickness of the structural repair coating.

Preferably the average grain size of the electrodeposited coating does not vary throughout the cross-sectional thickness of the coating. In other words the average grain size is substantially uniform throughout the thickness of the electrodeposited metal. By substantially uniform it is meant that the average

grain size is as uniform as humanly possible. Thus the invention preferably provides an equiaxed microstructure throughout the plated component, which is relatively independent of component thickness and structure. In a non-equiaxed microstructure there is a gradual increase in the average grain size throughout the thickness of the electrodeposited metal because of increasing grain size as a function of time during which electroplating takes place such that the first deposited metal has a relatively small grain size and metal deposited thereon has an increasingly larger grain size.

The present invention is particularly suitable for the repair of degraded metallic workpieces containing at least part of a tube, which are made of Fe, Cu and Ni based alloys and may be used to repair pipe containing, for example, Fe, Co, Cu, Ni, Mo, and Mn.

The electroformed coating layer may be a metal selected from the group consisting of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Pt, Rh, Ru, Sn, Mo, Mn, W, V and Zn. In addition, the electroformed coating layer may be an alloy as described above. For example alloys containing two or more of the above metals may further comprise alloying elements selected from the group consisting of B, C, P, S and Si.

The metal and metal alloys which are deposited may further comprise particulate additives to improve the physical characteristics of the metal. The particulate additives are incorporated into the metal or metal alloy during the electroplating procedure by, for example, suspending the particles in the plating solution so that the particles become entrapped in the electrodeposited metal or metal alloy. Suitable particulate additives include metal powders, metal alloy powders, metal oxide powders, nitrides, carbon (either graphite or diamond), carbides, MoS_2, and organic materials such as polytetrafluoroethylene (PTFE) and polymer spheres. Suitable metal oxides include oxides of Al, Co, Cu, In,

Mg, Ni, Si, Sn, V, and Zn. Suitable nitrides are nitrides of Al, B, C and Si. Suitable carbides include carbides of B, Cr, Bi, Si and W.

The metal or metal alloys which contain particulate additives as described above are referred to herein as metal matrix composites. The selection and amount of the particulates may be used to further enhance the coating material properties.

The patch formed in accordance with this invention preferably surrounds the degraded portion of the pipe to thereby form a patch in the form of a sleeve. The patches or sleeves may have a nonuniform thickness in order to enable thicker coating of damaged sections or sections particularly prone to corrosion such as those created by flow induced corrosion in elbows. The nonuniform thickness of the patch or sleeve may be accomplished by the appropriate selection and placement of consumable or inert anodes and possible shielding in the plating apparatus. This technique is particularly suitable to repair large outer diameter tubes.

It is also possible in the practice of this invention to electrodeposit age hardenable metallic coatings to form the patch. The strength and thermal stability of such a patch may be increased by a subsequent heat-treatment according to known procedures.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to better illustrate the invention by way of examples, descriptions are provided for suitable embodiments of the method/process/apparatus according to the invention in the case of small outer diameter feeder tubes (<6") in a nuclear reactor (Figure 1 to 3) and large outer diameter pipes (>1ft) used in e.g. gas pipelines (Figure 4).

Figure 1 is a sectional view through an axial plane of a feeder tube joint to a base plate illustrating a housing formed of two hinged sections sealing the degraded curved tube area to be plated, while providing fluid supply and electrical connections.

Figure 2 is a sectional view through an axial plane of a feeder tube joint to a base plate illustrating a housing containing two hinged sections sealing the degraded curved tube area to be plated against the base plate, while providing fluid supply and electrical connections.

Figure 3 is a sectional view through an axial plane of a T illustrating a housing formed of two sections sealing the degraded curved tube area to be plated, while providing fluid supply and electrical connections; and

Figure 4 shows a cross sectional view of a preferred embodiment of a brush plating apparatus used to repair a large outer diameter pipe.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

According to one aspect of the present invention the housing of the above-described plating cell is positioned and closed around a degraded portion of a pipe to provide a leak tight seal around the surface of the pipe which is to be plated. The fluid supply inlets and outlets are connected to a temperature controlled reservoir in order to enable the circulation of fluids to and from the pipe which is to be plated. Electrical connections are provided to the pipe and to one or several anodes which form the *in-situ* plating cell around the pipe. Prior to the circulation of plating solution through the plating cell, the pipe may be cleaned by circulating an aqueous alkaline cleaner followed by the circulation of rinse water through the plating cell. In addition, the surface of the portion of the pipe which is to be patched may be electropolished to eliminate

imperfections and may then be activated by circulating dilute mineral acid solution through the plating cell and then circulating rinsing water through the cell.

The plating cell is then used to electroform a structural layer of metallic material which an average grain size of less than 1000 nm on the external surface of the degraded portion of the pipe using electrodeposition (DC or pulse electrodeposition) at a deposition rate of at least 0.05 mm/h (preferably at least 0.075 mm/h and more preferably at least 0.1 mm/h) by flowing an aqueous electrolyte containing ions of the metallic material to be plated, passing single or multiple D.C. cathodic-current pulses between the anode and the portion of the pipe to be plated, i.e., the cathode, at a cathodic-current pulse frequency in the range of about 0 to 1000 Hz at pulsed intervals during which the current passes for a t_{on}-time period of at least 0.1 msec and does not pass for a t_{off}-time period in the range of about 0 to 500 msec, and passing single or multiple D.C. anodic-current pulses between the cathode and the anode at intervals during which the current passes for a t_{anodic}-time period in the range of 0 to 50 msec, the total duty cycle being in the range of 10 to 100%.

Instead of using the above-described plating cell to practice the invention, the desired *in situ* repair of the pipe or other workpiece may be accomplished by using the device described in figure 4. Thus, according to another aspect of the invention, the process comprises the steps of: assembling a selective plating apparatus employing an anode brush wrapped in an absorbent separator, connecting a fluid supply to the anode brush to enable the supply of fluids to the absorbent separator between the anode and the workpiece area to be plated, providing electrical connections to the workpiece to be plated and the anode brush forming the in-situ plating cell around the workpiece area to be plated, and electroforming a structural layer of metallic material with an average grain size which is equal to or less than 1,000 nm on the external surface area of the degraded section of the metallic

workpiece using electrodeposition (DC or pulse electrodeposition) at a deposition rate of at least 0.05 mm/h (preferably at least 0.075 mm/h and more preferably at least 0.1 mm/h) by supplying an aqueous electrolyte containing ions of said metallic material, placing the anode and the workpiece area to be plated, i.e. the cathode, in contact with said electrolyte by moving the anode brush over the workpiece area to be plated, passing single or multiple D.C. cathodic-current pulses between said anode and said workpiece area to be plated at a cathodic-current pulse frequency in a range of about 0 and 1000 Hz, at pulsed intervals during which said current passes for a t_{on}-time period of at least 0.1 msec and does not pass for a t_{off}-time period in the range of about 0 to 500 msec, and passing single or multiple D.C. anodic-current pulses between said cathode and said anode at intervals during which said current passes for a t_{anodic}-time period in the range of 0 to 50 msec, the total duty cycle being in a range of 10 to 100%.

In the process of the present invention periodic pulse reversal, a bipolar waveform alternating between cathodic pulses and anodic pulses, can be used. The anodic pulses can be introduced into the waveform before, after or in between the on pulse and/or before, after or during the off time. The anodic pulse current density is generally equal to or greater than the cathodic current density. The anodic charge (Q_{anodic}) of the "reverse pulse" per cycle is always smaller than the cathodic charge ($Q_{cathodic}$). Periodic pulse reversal has been found to be particularly effective in raising the temperature at which grain growth occurs and for leveling of the deposit.

According to a preferred embodiment of the invention, nanocrystalline deposits of the metals, metal alloys and metal matrix composites are obtained when process parameters such as current density, duty cycle, work piece temperature, plating solution temperature and solution circulation rates were varied over a wide range of conditions.

The following listing describes suitable operating parameter ranges for practicing the invention:

Average current density (if determinable, anodically or cathodically): 0.01 to 10A/cm^2, preferably 0.1 to 10A/cm^2, more preferably 1 to 10A/cm^2,

Total Duty Cycle: 10 to 100%

Frequency: 1 to 1000Hz

Electrolyte solution temperature: 0 to 85 °C

Electrolyte solution circulation/agitation rates: <10 liter per min per cm^2 anode or cathode area (0.0001 to 10 l/min.cm^2)

Work piece temperature: -20 to 85 °C

Cathodic pulse on-times of at least 0.1 msec, typically in the range from 0.1 to 50 msec, more preferably from 1 to 50 msec, off-times from 0 to 500 msec, preferably from 1 to 100 msec, and anodic pulse times range from 0 to 50 msec, preferably from 1 to 10msec. The total duty cycle, expressed as the cathodic on-times divided by the sum of the cathodic on-times, the off-times and the anodic times, ranges from 10 to 100% and is at least 10%, preferably at least 25%, more preferably at least 50% and most preferably at least 75%. The frequency of the cathodic pulses ranges from 0Hz to 1kHz, preferably from 1Hz to 1kHz and more preferably from 2Hz to 100Hz.

In the process of the present invention the electroformed metallic coatings optionally contain at least 5% by volume particulates, more preferable at least 10% by volume particulates and most preferably at least 20% by volume particulates. The particulates can be selected from the group of metal powders; metal alloy powders; metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn, V, and Zn; nitrides of Al, B, C and Si; C (graphite or diamond); carbides

of B, Cr, Bi, Si, W; MoS_2; and organic materials such as PTFE and polymer spheres. The particulate average particle size is typically below 10 microns, preferably below 1,000 nm (1mm), and more preferably below 500nm. The metal particulate and metal alloy particulate may be any of the metals and metal alloys which are electroplated.

In the process of the present invention the electrolyte preferably may be agitated by means of pumps, stirrers or ultrasonic agitation at rates of 0 to 750 ml/min/A (ml solution per minute per applied Ampere average current), preferably at rates of 0 to 500 ml/min/A.

In the process of the present invention optionally a grain refining/ stress relieving agent preferentially selected from the group of saccharin, coumarin, sodium lauryl sulfate, naphthalene trisulfonic acid and thiourea can be added to the electrolyte plating solution.

The present invention provides thick, structural coatings, having a thickness which is preferably at least 0.125mm, such as more than 0.25mm, more preferably at least 0.5mm, even more preferably at least 2.5mm, and most preferably at least 3mm on the outer surface of degraded tube or pipe sections, including elbows, tees, flanges and connections to e.g. base plates.

The electroformed metallic coatings of this invention have an average grain size equal to or less than 1 micron (1,000nm), preferably in the range of 10 to 750nm, more preferably between 30 and 500 nm and even more preferably between 50 and 300nm. In instances where low ductility is acceptable, the average grain size may be $\leq$ 100 nm.

To increase the part reliability, it is preferred to maintain the ratio between average thickness and average grain size of the coated layer of at least or greater than 1,000, preferably greater than 5,000, and more preferably greater than 10,000.

According to this invention, patches can be formed on the damaged areas without the need to electrodeposit an outer diameter sleeve on an entire tube section as e.g. in the case of a localized through-wall crack in a tube section which otherwise has no further damage, by the appropriate selection and placement of anodes in the plating apparatus, which is particularly suited to repair large outer diameter tubes.

The person skilled in the art of plating, in conjunction e.g. with U.S. patent no. 5,352,266 (1994) and in U.S. patent no. 5,433,797 (1995), the specifications of which are incorporated herein by reference, will know how to electrodeposit selected metals or alloys by selecting suitable plating bath formulations and plating conditions. Optionally solid particles can be suspended in the electrolyte and are included in the deposit to form a metal matrix composite.

Minimizing the thickness of structural repair coatings can be achieved by increasing the strength through grain size reduction. Since ductility is generally required in the electrodeposited metal patches of this invention, grain size refinement which produces average grain size values below 10nm do not necessarily provide the ideal structure. It has been determined that an average grain size of e.g. Ni-based coatings in the range of 50 to 250 nanometers provides a coating with suitable mechanical properties. Incorporating a sufficient volume fraction of particulates can be used to further enhance the coating material properties.

Depending on the requirements of the particular application, the material properties can also be altered e.g. by the incorporation of lubricants in the form of particulates (such as MoS_2, boron nitride and PTFE). Generally, the particulates such as particulate lubricants may be selected from the group of metal powders, metal alloy powders and metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn and Zn; nitrides of Al, B and Si; C (graphite or diamond); carbides of B, Si, W; MoS_2; and organic materials such as PTFE and polymer spheres.

Embodiments of the invention which use a plating cell are shown in figures 1-3. Fig. 4 illustrates an alternative embodiment which electroplates the metal patch without enclosing the degraded area of the workpiece (e.g., *in-situ* pipe) in a plating cell.

Figure 1 schematically shows the feeder tube (1) attached to a base plate (2). Flexible, split ring sections forming the anode (3) made of e.g. Ni, Co (soluble anodes) or Pt, Pt clad Nb, or Pt clad Ti (dimensionally stable anodes) are slipped over the feeder tube (1) and assembled to form the anode of the plating cell. A housing (4) containing two half shells is placed over the anode (3) and the tube section to be repaired and the housing is closed using a sealed hinged arrangement (5). The fluid connection (6) contains the electrolyte feed tube (7) and the electrical contact wire (19) to the anode (3). The electrolyte exits the housing (4) through the fluid connection port (6) and is circulated to a temperature-controlled tank (not shown) by a pump (not shown). The power supply (8) provides power to the anode (3) and the feeder tube (1), which forms the cathode. Electrical contact wire (20) connects the power supply to the feeder tube (1) which thereby functions as the cathode which is plated in the portion surrounded by the anode (3).

Figure 2 schematically shows the feeder tube (1) attached to a base plate (2). Anode-plates or -strips (3) made of e.g. Ni, Co (soluble anodes) or Pt, Pt clad Nb or Pt clad Ti (dimensionally stable anodes) are secured to the feeder tube (1) to form the anode of the plating cell. A housing (4) containing two half shells is placed over the anode (3) and the tube section to be repaired and the housing is closed using a sealed hinged arrangement (5). After closing the housing and inserting of a gasket (not shown) the housing is secured to the base plate by bolts (9). The electrolyte enters the housing (4) through the fluid inlet (10) and exits through the outlet (11). The electrolyte is circulated to a temperature-controlled tank (not shown) by a pump (not shown). The power supply (8) provides power to the anode (3) and the feeder tube (1) forming the cathode by wires (19) and (20) respectively.

Figure 3 schematically shows a T shaped feeder tube (1). Flexible, strips or plates (3) made of e.g. Ni, Co (soluble anodes) or Pt, Pt clad Nb or Pt clad Ti (dimensionally stable anodes) are secured to the feeder tube (1) to form the anode of the plating cell. A housing (4) containing two half shells is placed over the anode (3) and the tube section to be repaired and the housing is closed after inserting of a gasket (not shown) using bolts (12). The electrolyte enters the housing (4) through the fluid inlet (10) and exits through the outlet (11). The electrolyte circulated to a temperature-controlled tank (not shown) by a pump (not shown). The power supply (8) provides power to the anode arrangement (3) and the feeder tube (1) forming the cathode by electric wires (19) and (20) respectively.

According to a further preferred embodiment of the present invention it is also possible to produce nanocrystalline coatings by electroplating without the need to enclose the area of the article to be coated and form a plating bath around it. Brush or tampon plating is a suitable alternative, particularly when only a small portion of the work piece is to be plated. The brush plating

apparatus typically employs a soluble or dimensionally stable anode wrapped in an absorbent separator felt to form the anode brush. The brush is rubbed against the surface to be plated in a manual or mechanized mode and electrolyte solution containing ions of the metal or metal alloys to be plated is injected into the separator felt. An apparatus for carrying out this embodiment of the invention is shown in Fig. 4.

Figure 4 schematically shows the degraded area of a pipe component (1) to be plated which is connected to the negative outlet of the power source (8). The anode (3) consists of a handle (13) connected to a conductive anode brush (14). The anode contains channels (15) for supplying the electrolyte solution (16) from a temperature controlled tank (not shown) to the anode wick (absorbent separator) (17) . The electrolyte dripping from the absorbent separator (17) is optionally collected in a tray (18) and recirculated to the tank. The absorbent separator (17) containing the electrolyte (16) also electrically insulates the anode brush (14) from the workpiece (1) and adjusts the spacing between anode (3) and cathode (1). The anode brush handle (13) can be moved over the workpiece (1) manually during the plating operation. Alternatively, the motion can be motorized.

The following examples illustrate various embodiments of the invention. The electrolyte formulations described herein and in the examples are aqueous based.

EXAMPLE 1:

An elbow of SAE106 grade B 2 ½" schedule 80 pipe was fitted with an embodiment forming the plating cell described in Figure 1. After sealing the apparatus appropriate fluid connections were established. The surface of the tube was cleaned with a 10% solution of Soak 5000, a commercial alkaline

cleaner (Soak 5000) produced by Atotech, and rinsed with water. The surface was then subjected to an electropolishing step to eliminate imperfections, and then activated using a dilute mineral acid solution (20%HCl or H_2SO_4 for 10 minutes), followed by rinsing. Subsequently a 4mm thick layer of Ni (average grain size: 70nm) was plated onto the elbow using Pt-clad Nb ring sections as the anode material and the formulation and conditions listed below. After the plating was completed, the apparatus was drained, flushed with water three times and thereafter the apparatus was removed.

Electrolyte Formulation:

300 g/l nickel sulfate heptahydrate

40 g/l boric acid

0.1 g/l phosphorous acid

4 ml/l NPA-91 (organic surfactant)

Electrolyte temperature: 60°C

pH: ~2.5

Average cathodic current density: 0.13A/cm^2

T_{on}/ T_{off}: 8msec/ 2msec

Duty Cycle: 80%

Plating rate: ~0.005"/hr (0.13mm/hr)

Time needed to plate 4mm: 30hrs

Characteristics of electrodeposited metal:

Composition: Ni-0.2%P (99.8 wt. % Ni; 0.2 wt. % P)

Grain Size: 70nm

Hardness: 400 VHN (Vickers hardness)

Ratio of coating thickness to grain size: 57,143

EXAMPLE 2:

An elbow of SAE106 grade B 2 ½" schedule 80 pipe was fitted with an embodiment forming the plating cell described in Figure 2. Alkaline cleaning, rinsing, electropolishing, activation and rinsing were performed as indicated in Example 1. The plating cell contained a titanium housing and a Pt-clad Nb mesh anode conforming to the extrados enabling the selective plating of an area on the circumference of the elbow. Electroplating produced a patch which covered about 50% of the total pipe area enclosed by the plating cell and the average thickness of the coating was 4mm (average grain size: 200nm). The following conditions were used:

Electrolyte Formulation:

300 g/l nickel sulfate heptahydrate

40 g/l boric acid

0.1 g/l phosphorous acid

4 ml/l NPA-91 (surfactant)

Electrolyte temperature: 60°C

pH: ~2.5

Average cathodic current density: 0.10A/cm^2

T_{on}/ T_{off}: 8msec/ 2msec

Duty Cycle: 80%

Plating rate: ~0.004"/hr (0.10mm/hr)

Time needed to plate 4mm: 40hrs

Characteristics of electrodeposited metal:

Composition: Ni-0.15%P (99.85 wt. % Ni, 0.15 wt. % P)

Grain Size: 200nm

Hardness: 300 VHN

Ratio of coating thickness to grain size: 20,000

EXAMPLE 3:

The set up and pipe used were as described in Example 1. A nanocrystalline Co-TiO_2 nanocomposite of 0.25mm average coating thickness was then deposited onto the elbow section immersed in a modified Watts bath (i.e., the electrolyte formulation described in this example without the titania and particle dispersant) for cobalt using a soluble anode made of a cobalt plate and a Dynatronics (Dynanet PDPR 20-30-100) pulse power supply. The following conditions were used:

Electrolyte Formulation:

300g/l cobalt sulfate heptahydrate

45g/l cobalt chloride hexahydate

45g/l boric acid

2g/l sodium saccharinate

4ml/l NPA-91 surfactant

0-500g/l titania (<1mm particle size)

0-12g/l Niklad™ particle dispersant (supplied by MacDermid Inc.) (a surfactant for dispersing the titania particles)

Electrolyte temperature: 60°C

pH: ~2.5

Average cathodic current density: 0.125A/cm^2

T_{on}/ T_{off}: 2msec/ 6msec

Duty Cycle: 25%

Plating rate: ~0.0016"/hr (0.04mm/hr)

Time needed to plate 0.25mm: 6¼ hrs

A series of electrodeposits were produced on a number of tube elbow-sections using the modified Watts bath with the addition of TiO_2 particles (particle size <1 mm) ranging from 50g/l to 500g/l. Table 1 illustrates the properties of the deposits. The ratio of coating thickness to grain size is between 14,700 and 16,700.

Table 1: Co-TiO_2 nanocomposite properties

Sample	Bath Concentration TiO_2 [g/l]	Bath Concentration Dispersant [g/l]	Grain Size of Co deposit [nm]	TiO_2 Fraction in Deposit [Volume %]	Micro-hardness [VHN]
Control	0	0	16	0	490
1	50	0	15	19	507
2	100	1.5	15	23	521
3	200	3	17	32	531
4	300	6	17	38	534
5	500	12	16	37	541

EXAMPLE 4:

T-sections of an Alloy 600 (UNS N06600) tube (OD=1.9cm) were fitted with an embodiment forming the plating cell described in Figure 3. The plating cell contained two titanium housing plates conforming to the geometry of the T-section enabling the plating of a "reinforcement" layer on one side of the connecting tube and around the joint area. The patch covered about 65% of the total T area enclosed by the plating cell. A 1mm thick layer of Co-2.5wt%P (97.5 wt. % Co, 2.5 wt. % P) (average grain size: 10nm, 650VHN) was plated onto the T-section using the formulation and conditions listed:

Electrolyte Formulation:

250g/l cobalt chloride

20g/l phosphoric acid

8g/l phosphorous acid

Electrolyte temperature: 75°C

pH = 1.75

Average cathodic current density: 0.150A/cm^2

T_{on} / T_{off}: 2msec/ 6msec

Plating rate: 0.005"/hour

Time needed to plate 1mm: 8 hours

Characteristics of electrodeposited metal:

Composition: Co-2.5%P

Grain Size: 10nm

Hardness: 650 VHN

Ratio of coating thickness to grain size: 100,000

After plating the section was heat treated at 400°C for 5min. The hardness of the coating was increased to 900VHN.

EXAMPLE 5:

A 6 in^2 area degraded by a localized crack in a mild steel pipe (outer diameter=3ft) was repaired using the selective plating set-up described in Figure 4. A DC power supply was employed. Standard alkaline electro cleaners were used to remove any dirt, oil or grease from substrate (i.e., the external surface of the pipe). Thereafter a standard activation solution was used to remove any oxides, corrosion products or otherwise contaminated surface material, which could adversely affect coating adhesion. Using the anode brush with manual operation a nanocrystalline Ni~0.6wt%P (99.4 wt. % Ni, 0.6 wt. % P) (average grain size: 13nm, 780VHN) patch was deposited onto the degraded section until the original thickness was restored. Plating was continued and an area of about 10 in^2 was coated to form a patch extending

about 0.25mm from the pipe surface using the following conditions:

Electrolyte Formulation:

137 g/l nickel sulfate heptahydrate

36 g/l nickel carbonate

4 g/l phosphorus acid

2 g/l sodium saccharinate

Electrolyte temperature: 65°C

Phosphoric acid to adjust pH to 1.5

Average cathodic current density: 0.1A/cm^2

Plating rate: 0.05mm/hr

Composition: Ni-0.6%P (99.4 wt. % Ni, 0.6 wt. % P)

Grain Size: 13nm

Hardness: 780 VHN

Ratio of coating thickness to grain size: 19,230

Anode versus cathode linear speed: 125cm/min

Electrolyte circulation rate: 10 ml solution per min per cm^2 anode area or 440 ml solution per min per Ampere average current applied

CLAIMS

1. A method for patching a degraded portion of a metallic workpiece which comprises electroplating a reinforcing metallic patch on an exterior surface of said workpiece wherein said patch covers said degraded portion of said workpiece without covering at least a portion of a non-degraded portion of said workpiece; said electroplating being conducted under electroplating conditions whereby electrodeposited metal of said metallic patch has an average grain size of 1000 nm or less.

2. The method of claim 1 wherein said workpiece is a pipe.

3. The method of claim 2 wherein the pipe is connected to an apparatus for the conveyance of fluid and said patch is formed in situ without removing the pipe from said apparatus.

4. The method of claim 3 wherein the electroplating is performed by surrounding the exterior degraded portion of the pipe with an electroplating cell through which electroplating solution containing ions of the metal to be electrodeposited is circulated whereby said solution contacts said exterior degraded portion of the pipe while the cell is operated to electrodeposit said metal onto said exterior degraded portion of said pipe to thereby form said patch;

said electroplating cell comprising:

a housing which surrounds the exterior degraded portion of said pipe; at least one anode within said housing; electrical connections which connect said at least one anode to an electric power source required for electroplating said metal and which connect said power source to said pipe whereby said pipe is a cathode during said electroplating.

5. The method of claim 4 wherein said housing comprises two sections and said sections of said housing are assembled around said exterior degraded portion of said pipe to form a watertight seal around said pipe; and said housing comprises a fluid inlet for introducing electroplating solution into said plating cell and a fluid outlet for removing electroplating solution from said cell whereby said electroplating solution is circulated through said plating cell by flowing the solution from the inlet to the outlet.

6. The method of claim 5 wherein said sections of said housing are joined together along one side thereof by a hinge whereby said housing can be opened and closed around said exterior degraded portion of said pipe and said housing is assembled around said exterior degraded portion of said pipe by closing said housing around said pipe.

7. The method of claim 6 which further includes regulating the temperature of said electroplating solution circulating through said plating cell to enhance the electroplating of said reinforcing metallic patch.

8. The method of claim 7 which further includes agitating the electroplating solution circulating through said plating cell.

9. The method of claim 3 wherein said electroplating is conducted under electroplating conditions whereby electrodeposited metal of said metallic patch has an average grain size in the range of 10-750 nm.

10. The method of claim 9 wherein the average grain size is in the range of 30-500 nm.

11. The method of claim 10 wherein the average grain size is in the range of 50-300 nm.

12. The method of claim 11 wherein the average grain size is in the range of 10-100 nm.

13. The method of claim 3 wherein said reinforcing metallic patch is electroplated to an average thickness of at least 0.125 mm.

14. The method of claim 3 wherein said pipe comprises a Fe, Cu or Ni based alloy.

15. The method of claim 3 wherein said electrodeposition provides an equiaxed microstructure throughout the electrodeposited metal wherein the average grain size is substantially uniform throughout the electrodeposited metal.

16. The method of claim 13 wherein said electroplating is conducted to produce an average grain size of said electrodeposited metal such that the ratio of said thickness to said average grain size is at least 1000.

17. The method of claim 3 wherein said electrodeposited metal is selected from the group consisting of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Pt, Rh, Ru, Sn, Mo, Mn, W, V, and Zn, or said metal is an alloy comprising one or more metals selected from the group consisting of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Pt, Rh, Ru, Sn, Mo, Mn, W, V, and Zn alloyed with an alloying element selected from the group consisting of B, C, P, S and Si, or said metal is an alternative alloy comprising two or more metals selected from the group consisting of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Pt, Rh, Ru, Sn, Mo, Mn, W, V, and Zn, wherein said alternative alloy optionally further comprises an alloying element selected from the group consisting of B, C, P, S and Si.

18. The method of claim 17 which further comprises incorporating particulate material into said electrodeposited metal during said electroplating to form a metal matrix composite, said particulate material being selected from the group consisting of metal powder, metal alloy powder, metal oxide, nitride powder, carbon powder, carbide powder, MoS_2 and organic material wherein:

said metal oxide is metal oxide of metal selected from the group consisting of Al, Co, Cu, In, Mg, Ni, Si, Sn, V and Sn;

said nitride is a nitride of an element selected from the group consisting of Al, B, C, and Si;

said carbide is a carbide of an element selected from the group consisting of B, Cr, Bi, Si and W;

said organic material is selected from the group consisting of polymer spheres and particulate polytetrafluoroethylene; and

said carbon is graphite or diamond.

19. The method of claim 17 wherein said electroplating is conducted from an electroplating solution which includes grain refining/stress relieving agent selected from the group consisting of saccharin, coumarin, sodium lauryl sulphate, naphthalene trisulfonic acid and thiourea.

20. The method of claim 18 wherein said particulate material has an average particle size of less than 10 microns.

21. The method of claim 4 wherein said electrodeposition takes place using DC or pulse electrodeposition at a deposition rate of at least 0.05 mm/hour.

22. The method of claim 20 wherein said electrodeposition is accomplished by passing single or multiple DC cathodic-current between the anode and said cathode at a cathodic-current pulse frequency in the range of about 0 to 1000 Hz at pulsed intervals during which the current passes for a t_{on}-

time period of at least 0.1 msec and does not pass for a t_{off}-time period in the range of 0 to 500 msec, and passing single or multiple DC anodic-current pulses between the cathode and the anode at intervals during which the current passes for a t_{anodic}-time period in the range of 0 to 50 msec, the total duty cycle being in the range of 10% to 100%.

23. The method of claim 3 wherein said electroplating comprises:

connecting said pipe to a negative outlet of an electric power source whereby said pipe functions as a cathode during said electroplating;

supplying electroplating solution to an anode wick which is connected to a conductive anode brush, said anode brush being connected to a power outlet of an electric power source;

contacting said wick with said exterior portion of said pipe to be patched and moving said wick in contact with said pipe over a portion of said pipe which is to be covered with said reinforcing metallic patch, whereby said electroplating solution from said wick bathes the portion of the pipe to be patched so that said reinforcing metallic patch is electroplated on the exterior surface of said pipe.

24. Process for in situ electroforming a structural reinforcing layer of a thickness of at least 0.125 mm of selected metallic material coated on an external surface area of a degraded section of a metallic workpiece containing Fe, Co, Cu, Ni, Mo, Mn comprising:

(i) assembling a housing in the vicinity of the workpiece area to be plated,

(ii) positioning and closing the housing to provide a leak tight seal around the surface area of the workpiece to be plated,

(iii) connecting fluid supply inlets and outlets to a temperature controlled reservoir to enable the circulation of fluids to and from the workpiece to be plated,

(iv) providing electrical connections to the workpiece to be plated and to one or several anodes forming the in-situ plating cell around the workpiece

area to be plated, so that said workpiece becomes a cathode during said electroforming

(v) electrodepositing a structural layer of metallic material with an average grain size of less than 1,000 nm on the external surface area of the degraded section of the metallic workpiece using electrodeposition at a deposition rate of at least 0.05 mm/h, by flowing an aqueous electrolyte containing ions of said metallic material, providing the anode and the workpiece area to be plated in contact with said electrolyte, passing single or multiple D.C. cathodic-current pulses between said anode and said workpiece area to be plated at a cathodic-current pulse frequency in a range of about 0 and 1000 Hz, at pulsed intervals during which said current passes for a t_{on}-time period of at least 0.1 msec and does not pass for a t_{off}-time period in the range of about 0 to 500 msec, and passing single or multiple D.C. anodic-current pulses between said cathode and said anode at intervals during which said current passes for a t_{anodic}-time period in the range of 0 to 50 msec, a total duty cycle being in a range of 10 to 100%.

25. Process for in situ electroforming a structural reinforcing layer of a thickness of at least 0.125 mm of selected metallic material coated on an external surface area of a degraded section of a metallic workpiece containing Fe, Co, Cu, Ni, Mo, Mn comprising:

(i) assembling a selective plating apparatus employing an anode brush wrapped in an absorbent separator,

(ii) connecting a fluid supply to the anode brush to enable the supply of fluids to the absorbent separator between the anode and the workpiece area to be plated,

(iii) providing electrical connections to the workpiece to be plated and the anode brush forming the in-situ plating cell around the workpiece area to be plated, and

(iv) electrodepositing a structural layer of metallic material with an average grain size of less than 1,000 nm on the external surface area of the degraded section of the metallic workpiece using electrodeposition at a deposition rate of at least 0.05 mm/h, by supplying an aqueous electrolyte containing ions of said metallic material, providing the anode and the workpiece area to be plated in contact with said electrolyte by moving the anode brush over the workpiece area to be plated, passing single or multiple D.C. cathodic-current pulses between said anode and said workpiece area to be plated at a cathodic-current pulse frequency in a range of about 0 and 1000 Hz, at pulsed intervals during which said current passes for a t_{on}-time period of at least 0.1 msec and does not pass for a t_{off}-time period in the range of about 0 to 500 msec, and passing single or multiple D.C. anodic-current pulses between said cathode and said anode at intervals during which said current passes for a t_{anodic}-time period in the range of 0 to 50 msec, a total duty cycle being in a range of 10 to 100%.

26. Process as claimed in claim 24 or 25, characterized in that the single or multiple D.C. cathodic-current pulses between said anode and said cathode have a peak current density in the range of about 0.01 to 10 A/cm^2.

27. Process as claimed in claim 26, characterized in that the peak current density of the cathodic-current pulses is in the range of about 0.1 to 10 A/cm^2.

28. Process as claimed in claim 24, characterized in that said selected metallic material is (a) a pure metal selected from the group consisting of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Rt, Rh, Ru, Mo, Mn, Sn, V, W, Zn, or (b) an alloy containing at least one of the elements of group (a) and alloying elements selected from the group consisting of C, P, S and Si.

29. Process as claimed in claim 24, characterized in that the t_{on}-time period is in the range of about 0.1 to about 50 msec, the t_{off}-time period is in the range of about 1 to 100 msec and the t_{anodic}-time period is in the range of about 1 to 10 msec.

30. Process as claimed in claim 24, characterized in that the duty cycle is at least 25%.

31. Process as claimed in claim 24, characterized in that the cathodic-current pulse frequency ranges from 2 Hz to 100 Hz.

32. Process as claimed in claim 24, characterized in that the deposition rate is at least 0.075 mm/h.

33. Process as claimed in claim 24, characterized in that the electrolyte is agitated by means of pumps, stirrers or ultrasonic agitation at rates of 0 to 750 ml/min/A (ml solution per minute per applied Ampere average current).

34. Process as claimed in claim 24, characterized in that said electrolyte contains a stress relieving/grain refining agent selected from the group of saccharin, coumarin, sodium lauryl sulfate, naphthalene trisulfonic acid and thiourea.

35. Process as claimed in claim 24, characterized in that said electrolyte contains particulate additives in suspension selected from pure metal powders, metal alloy powders or metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn, V and Zn, nitrides of Al, B and Si, carbon C (graphite or

diamond), carbides of B, Bi, Si, W, or organic materials such as PTFE and polymers spheres, whereby the electrodeposited metallic material contains said particulate additives.

36. Process as claimed in claim 35, characterized in that the electrodeposited metallic material contains at least 5% by volume of said particulate additives.

37. Process as claimed in claim 35, characterized in that the electrodeposited metallic material contains at least 10 % by volume of said particulate additives.

38. Process as claimed in claim 35, characterized in that the electrodeposited metallic material contains at least 20% by volume of said particulate additives.

39. Process as claimed in claim 35, characterized in that the particulate additives average particle size is below 10 µm.

40. Process as claimed in claim 24, characterized in that the thickness of the reinforcing layer is at least 0.5 mm.

41. Process as claimed in claim 24, characterized in that the average grain size of the deposited layer is equal to or smaller than 1000 nm and that the ratio between the thickness and the average grain size of the coated layer is greater than 1,000.

42. Process as claimed in any claim 24, characterized in that the coated layer has an equiaxed micro structure.

43. Process as claimed in claim 24, characterized by maintaining said electrolyte at a temperature in the range between 0 to 85°C.

44. Process as claimed in claim 24, characterized by cleaning, electropolishing or striking the workpiece.

45. Process as claimed in claim 24, characterized by electroforming age hardenable metallic coatings and increasing the strength and thermal stability thereof by a subsequent heat-treatment.

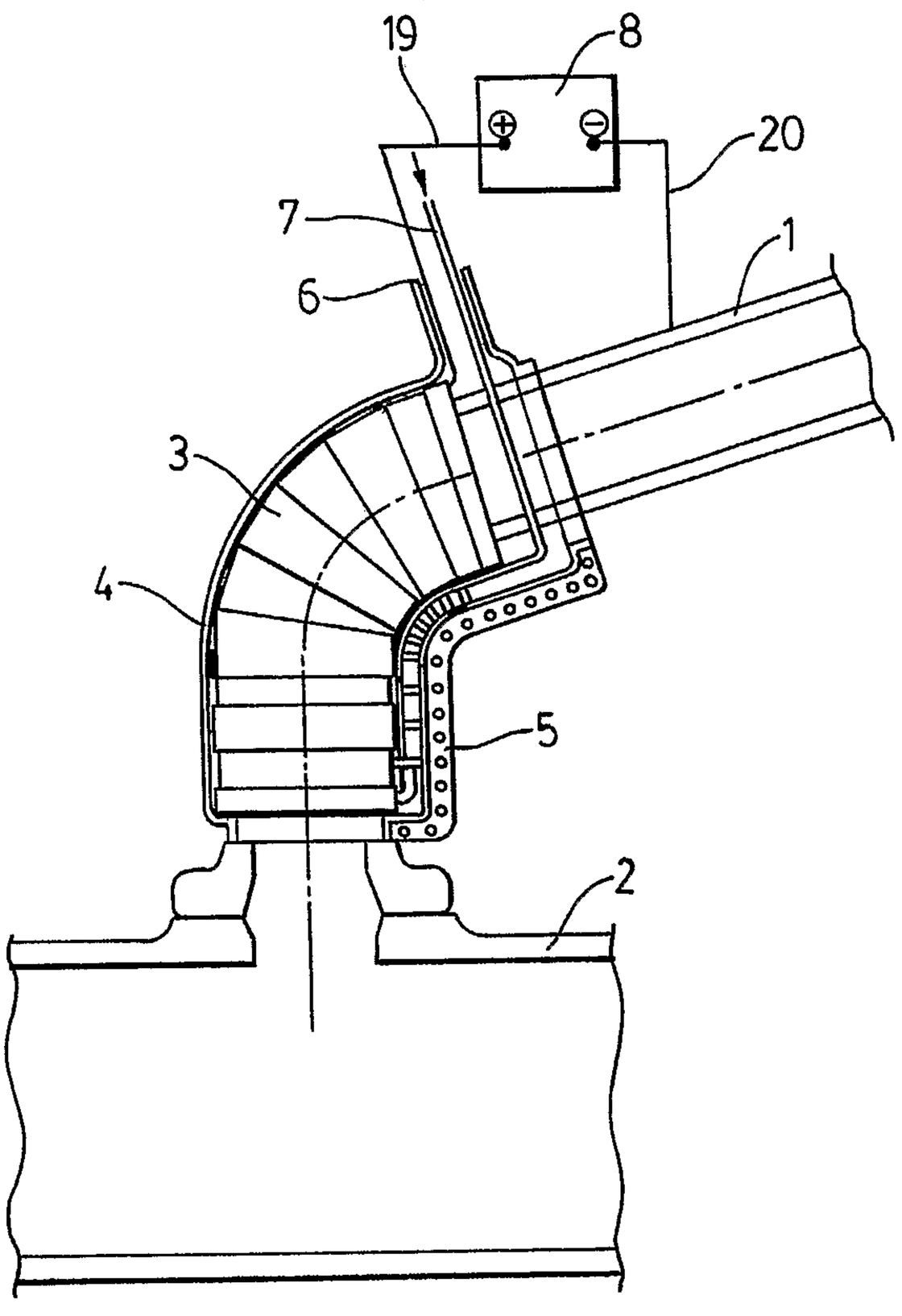


FIG. 1

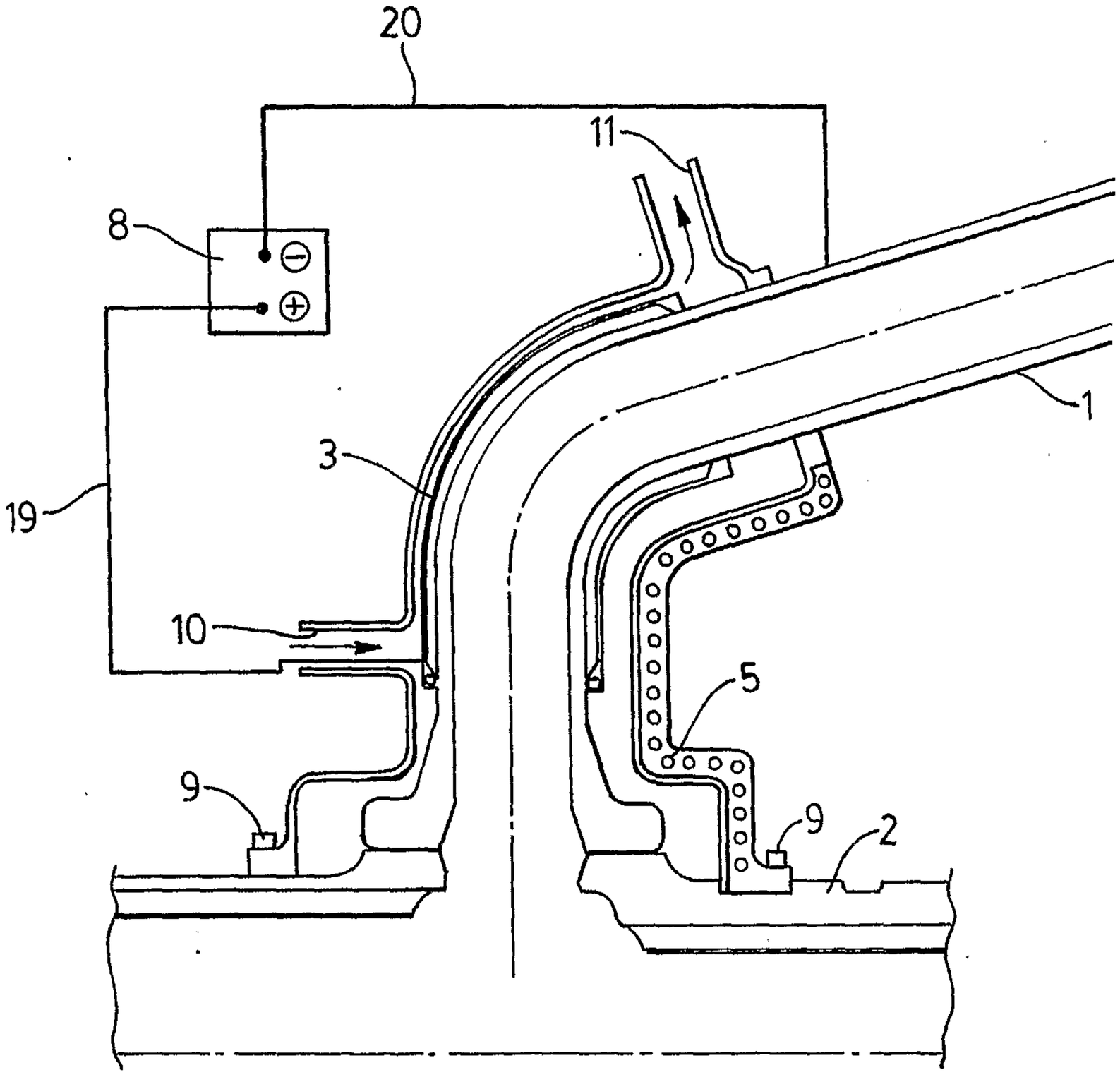


FIG. 2

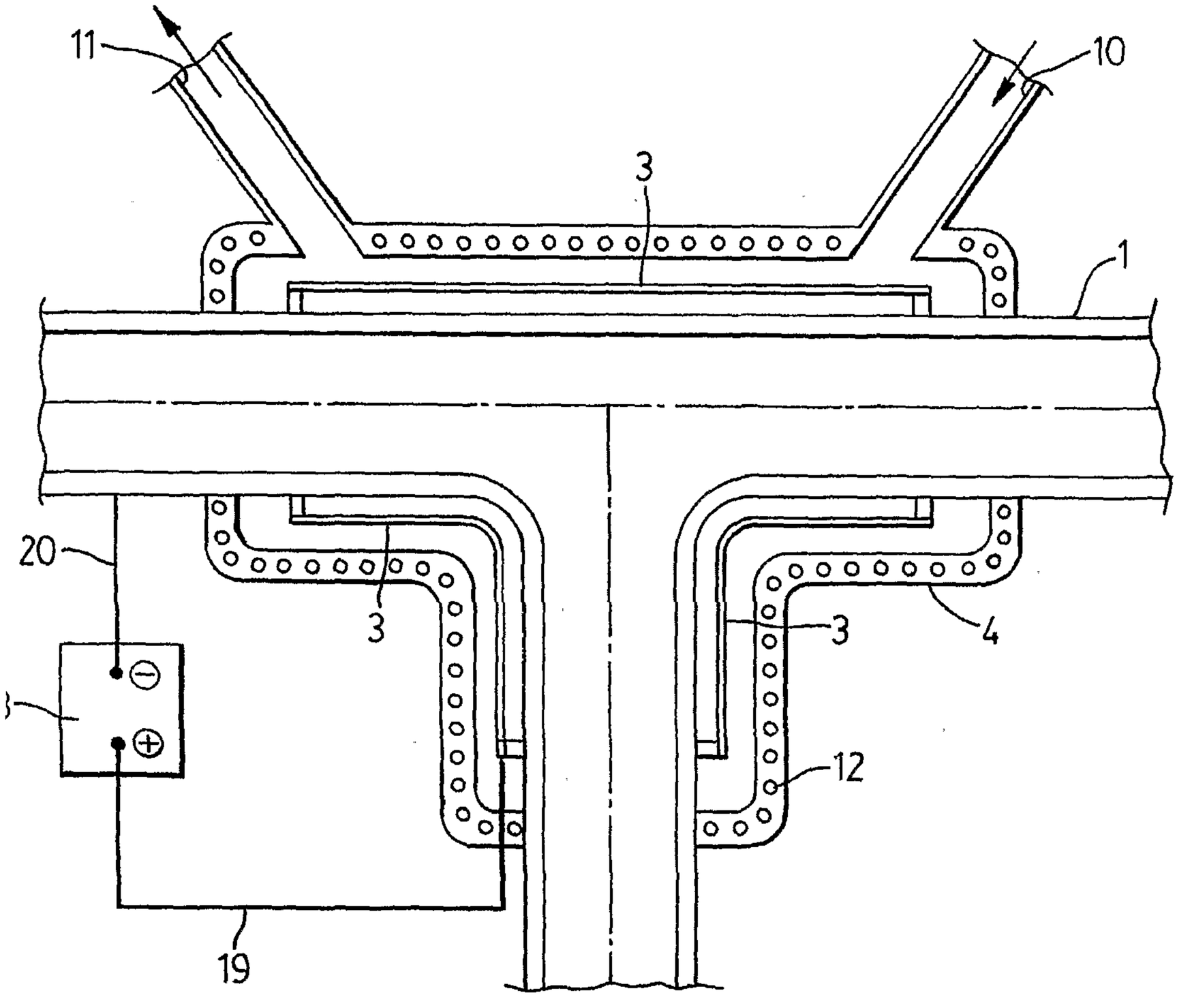


FIG. 3

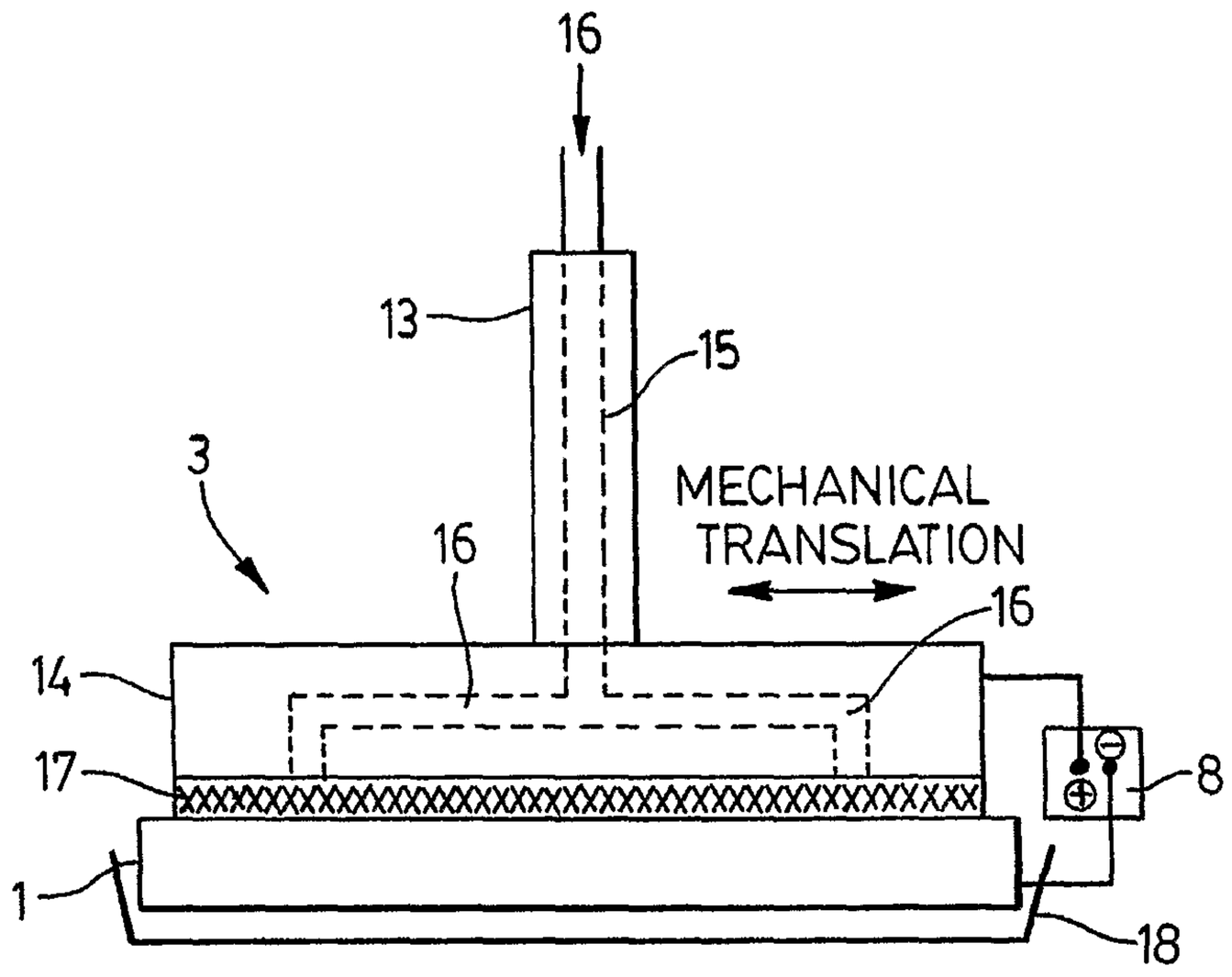
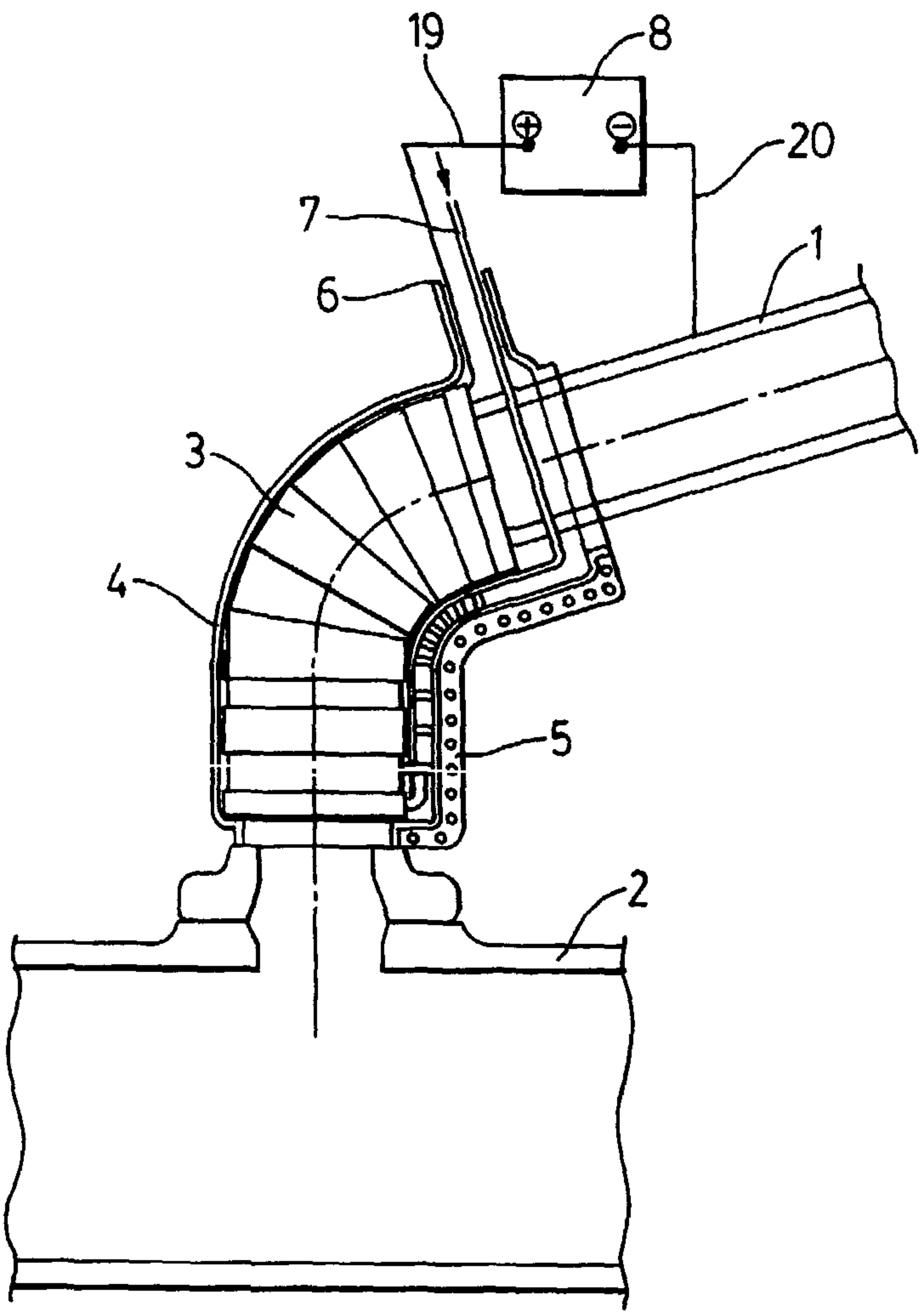


FIG. 4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