Sept. 4, 1973 J. G. LUCAS ET AL 3,756,937

APPARATUS FOR AN ELECTROCHEMICAL MILLING PROCESS

Filed June 24, 1971 2 Sheets-Sheet 1

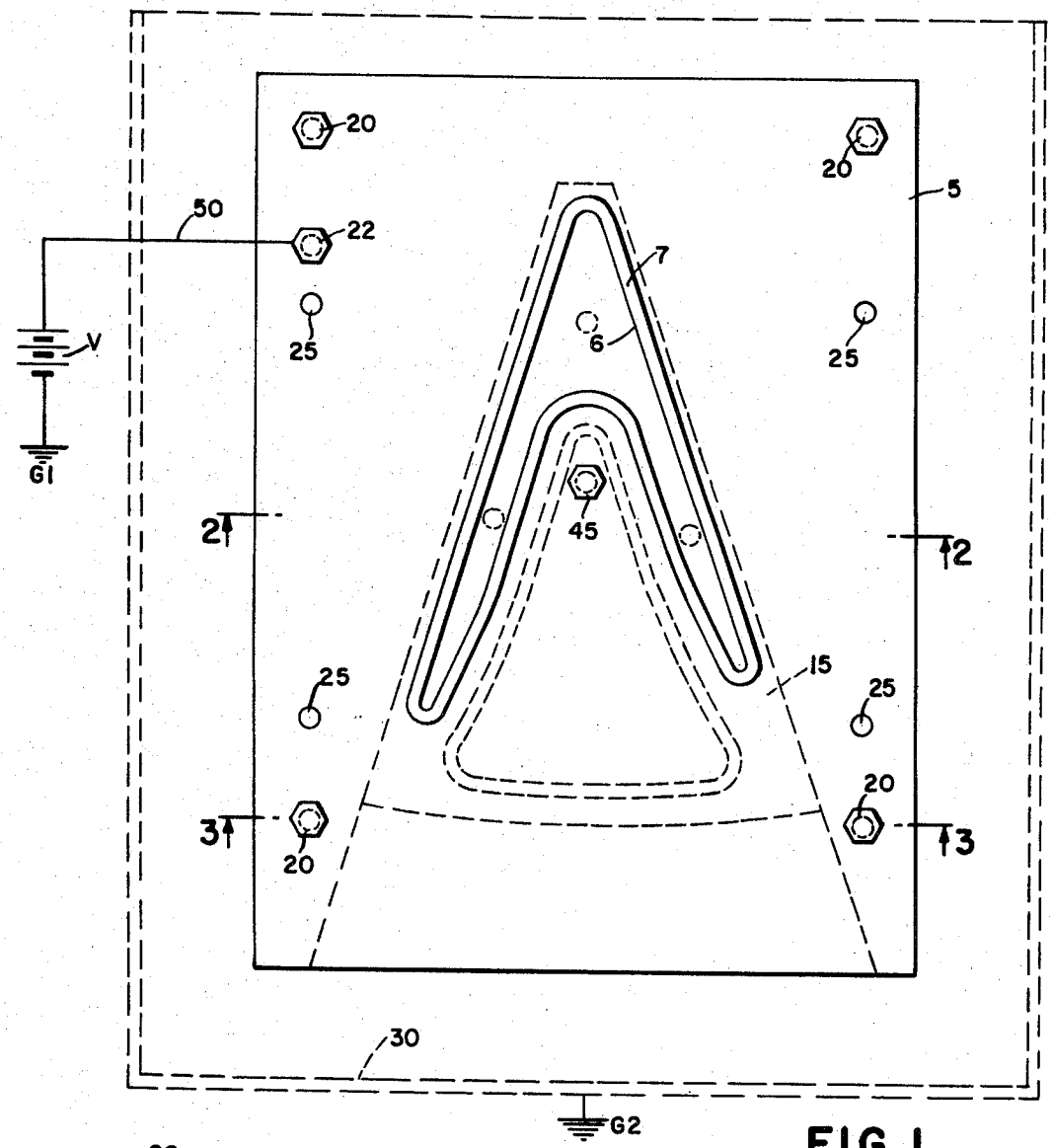


FIG. 1.

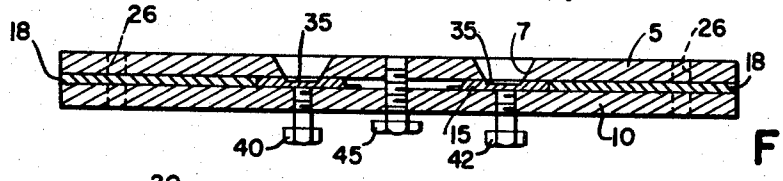


FIG. 2.

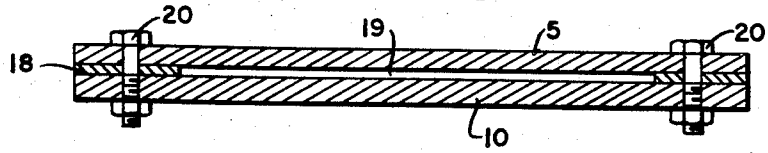


FIG. 3.

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APPARATUS FOR AN ELECTROCHEMICAL MILLING PROCESS

Filed June 24, 1971 2 Sheets-Sheet 2

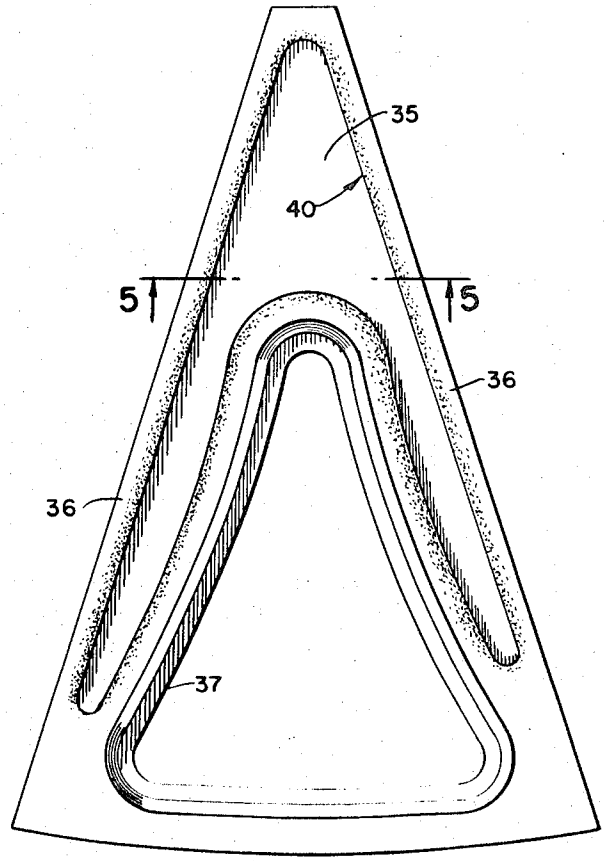


FIG. 4.

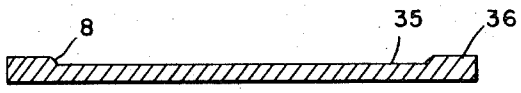


FIG. 5.

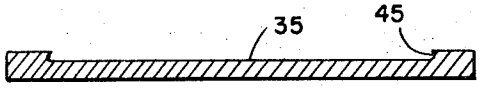


FIG. 6.

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APPARATUS FOR AN ELECTROCHEMICAL MILLING PROCESS

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Continuation-in-part of abandoned application Ser. No. 638,298, May 15, 1967. This application June 24, 1971, Ser. No. 156,372

Int. Cl. B23p 1/02

U.S. Cl. 204—224 M 7 Claims

ABSTRACT OF THE DISCLOSURE

A process and apparatus for the selective removal of metal from a corrosion resistant metal piece by electrochemical milling by covering the piece with an aluminum or titanium electrically conductive mask which is provided with a protective surface through anodization during the process, the non-masked, etched surfaces of the metal piece being electrochemically dissolved to a predetermined depth.

This application is a continuation in part of application Ser. No. 638,298 filed May 15, 1967, now abandoned.

This invention is directed to a novel process and apparatus for electrochemical milling of workpieces, particularly articles of a ferrous nature. Actually, the process is most adaptable to the electrochemical milling of corrosive resistant ferrous alloys as stainless steels, commonly used in the manufacture of such commercial equipment as heat exchangers and like apparatus, wherein milling is desired within fine tolerances to provide internal cavities or depressions of predetermined size and shape.

The process may be briefly summarized as one wherein the corrosion resistant workpiece is initially masked prior to submersion in the electrolyte by a valve metal mask or overlay having cut out portions therein representing the area in the piece to be milled. The essence of the invention is that the same electrolytic action which serves to mill the workpiece renders the mask resistant, so that only the unmasked area is milled.

It is well known that certain valve metals, including aluminum and titanium, are subject to anodic oxidation, or become anodized when subjected to certain acidic reactants. The term "anodized" is herein used to characterize the hard, noncorroding oxide film which is deposited on the surface of such metals. The term "valve metal" as used herein is defined as including any metal having characteristics such that the metal becomes anodized when immersed in an acidic electrolyte through which current is passed and wherein the oxide of said metal resulting from such oxidation is substantially nonconductive and passivated with respect to the electrolytic action. Such metals include aluminum and tantalum. Apparently because of this characteristic of these metals in particular, it is characteristic of the art that such elements or the alloys thereof have been discouted as being useful as anodes in electrolytic baths, particularly where the electrolyte is one such as sulphuric acid, for such an anode immediately becomes anodized and its surface conductive capacity, as an anode, thereby immediately passivated, immunized or destroyed. However, in the instant invention advantage is taken of this phenomenon by utilizing a mask made of valve metal and held in tight surface to surface and fluid excluding contact with the workpiece with resultant efficient current flow through the interior of both mask and piece, whereas the exposed surface of the mask, in practically immediately becoming anodized when immersed in the electrolyte, becomes immune to attack by the electrolytic bath. The result

is twofold: Efficient current flow through mask and piece, as indicated above, and secondly, confinement of electrolytic conduction, electrolysis or ion travel to the precise areas desired, and with greater concentration or effect within such areas where milling is to be achieved. As stated, under these circumstances the workpiece itself functions as the anode.

The process of our invention, extremely efficient in the commercial practice thereof, is considerably less expensive than either the mechanical or machining method of milling, or mere chemical milling with its comparatively costly masking methods and as well, complex chemical solutions necessitated by such a practice. The process and masking materials employed in accordance with this invention contemplate utilization of materials which by their very nature result in a dissolving effect on the exposed surfaces of the piece (here corrosion resistant steel) and a passivity or anodic film formation on the masking fixture whether it be an aluminum, titanium alloy or any other valve metal. Thus the fixtured part is subjected to the electrochemical action of a typical sulphuric acid anodizing bath under those conditions of voltage, temperature and solution makeup which are usually practiced in the anodizing art. At any rate, during such process the steel piece is selectively dissolved away to the desired depth while the rack or fixture, performing both as an electrical conductor and as a preformed mask, is itself protected from metal loss by the formation of the referred to anodic coating over its exposed surface.

It is, accordingly, a primary objective of our invention to provide an electrochemical milling process wherein valve metals such as aluminum or titanium, or alloys thereof, are utilized as masking or overlay materials, these forming the conductor to the anode, but at the same time these, at the very inception of the milling procedure being immediately anodized upon their exterior or exposed surfaces by action of the electrolyte so that not only is full current flow to those areas to be milled obtained but, also, the protective film of oxide resultantly formed upon the exposed surfaces of such aluminum or titanium overlay has the effect of concentration of the current or concentration of ion flow to those areas in the piece directly exposed to the electrolyte and sought to be electrochemically milled.

It is an additional object of the invention to provide a mask for use in electrochemical milling of the type herein described wherein, either by use of a heavy metal mask of aluminum or titanium, or a coating of the surface of the workpiece with such a metal or alloys thereof, substantial undercutting is eliminated in the sense that the opening or openings in the mask representing the portions of the workpiece to be milled substantially parallel, in diameter size, the size of the milled area.

It is a further object of the invention to provide a preformed, rigid mask of substantial thickness, so mounted with regard to the workpiece to be milled that there is little or no leakage of electrolyte between mask and workpiece. Any slight leakage that occurs results in the immediate anodization of the mask at the leakage area with the resultant oxide formation rendering any area between piece and mask inactive insofar as any electrochemical milling therein be concerned; the practical result is that this natural effect reduces or eliminates any substantial undercut.

It is another object of the invention to provide a process of electrochemical milling wherein the overlay or mask takes the form of a deposited surface of aluminum or titanium upon the workpiece. The latter is of minimal thickness, resulting in an even sharper definition of the milled area with even lesser undercutting thereof.

In such practice the deposited film of aluminum or titanium can be easily removed, after milling, by subjection to strong basic or acidic reactants.

A further objective of the invention is the provision of a process for electro milling wherein a combination mask may be utilized; in this regard a preformed, rigid mask comprised of a relatively thick valve metal, such as aluminum or titanium, can surmount an underlying layer of deposited material of the same characteristic, this combination resulting in an even greater lessening of undercutting in the milled area.

Other objects and advantages of the instant process will be understood by those skilled in the art from consideration of the following more detailed description thereof. In connection therewith, the attached figures demonstrate a means for practicing the inventive process utilizing the so-called "heavy" or permanent type of mask. In these figures:

FIG. 1 is a top plan view of a solid mask superimposed over the material to be milled, which latter material is securely fastened in between the mask and a lower imperforate piece of the same or similar material, the workpiece being so clamped between same as to be in solid contact with the aluminum or titanium overlay, the latter thereby conducting current from an outside source through the interior thereof and to the piece to be milled, which piece in this arrangement represents the anode;

FIG. 2 is a section view taken on the line **2—2** of FIG. 1;

FIG. 3 is a section view taken on the line **3—3** of FIG. 1;

FIG. 4 is a top plan view of a workpiece which has been milled through the practice of our process, indicating the configuration cut therein and, also, the slight areas adjacent the area which has beetn milled where some leakage of electrolyte has occurred but where no milling has occurred because of the anodizing action in such areas;

FIG. 5 is a section view taken on line **5—5** of FIG. 4, showing, in exaggerated form, the depth of the milling cut and, also, the absence of substantial undercutting at the edges thereof; and

FIG. 6 illustrates diagrammatically the nature of a so-called "undercut" or inwardly beveled edge which is undesired and which is substantially prevented by the practice of the instant process.

FIG. 1 represents an assembly useful for accomplishing a method of the invention wherein the overlay **5** consists of an aluminum or titanuim piece having cut therein, as at **6**, an opening or pattern of the configuration desired to be milled in the workpiece. The edges of this opening **6** are beveled, as at **7**, and within prescribed ranges of angularity, as will hereinafter be described. The piece to be milled is indicated at **15** and it is placed in between the overlay **5** and an opposite plate **10** which may or may not be of the same material as the overlay so long as it is passive toward the electrolyte. This back plate **10**, however, is preferably of an exterior configuration to match the exterior rectangular configuration of the overlay **5**.

The workpiece **15** is thus compressed between these two members **5** and **10**, the latter being held together in more or less permanent fashion by bolts **20** with an intermediate shim or gasket **18** spaced therebetween, thus leaving an interior space **19** for insertion of the part to be milled. Such member **18** is preferably of the same metal as the overlay but may also be of a material passive to the electrolyte. It may have cut therein a configuration more or less matching the exterior configuration of the workpiece. The space **19** provided by the shim **18** sandwiched between **5** and **10** is thus such that it will permit insertion and removal of the work piece, the latter in this embodiment of the invention having the configuration shown in dotted line in FIG. 1. As stated, gasket **18** may be configured to complement the external "V" shape of the piece **15** as it is here shown. Thus space **19** will permit ready insertion of the workpiece prior to milling and removal therefrom after milling.

These two plates **5** (the overlay) and underlying member **10** are further precisely located with regard to each other by a series of pins **25** positioned in appropriate apertures in elements **5**, **18** and **10**, respectively, so that the parts of the assembly prior to immersion in the electrolytic bath are accurately and precisely located with respect to each other in the manner shown.

A close fitting in face to face relationship between element **5**, workpiece **15** and lower plate **10** is desired, this in order that any substantial leakage of electrolyte is prohibited, the electrolytic action thus being confined only to the area outlined by the configuration **6** in the overlay. To this end, suitable bolts **40** and **42** are so located as to exert pressure upon the underside of the workpiece, and as indicated in FIG. 2. These, when threaded towards the part to be milled will exert a pressure thereon. To further insure adequate pressure and completely tight face to face contact between workpiece and overlay, an additional center bolt **45** is employed, this again, when such is taken up, compressing the two elements **5** and **10** together with the workpiece **15** positioned therebetween.

A suitable container for the electrolytic bath, made of material immune to electrolytic action, is diagrammatically indicated in dotted line at **30**. The assembly as heretofore described is now placed in the bath and subjected to the electrochemical milling action. Sulphuric acid, in the case of employing either an aluminum or titanium mask or overlay is preferably used as the electrolytic solution to mill the involved ferrous material, as stainless steel, to the pattern represented by the configuraion **6**. A voltage from a source V is fed to the aluminum overlay **5** through line **50**, the latter being firmly connected to a bolt **22**, threaded directly into the aluminum or titanium overlay **5**. The voltage source is grounded as at G_1 and, of course, the metal container for the bath, **30**, is similarly grounded, as at G_2.

With this arrangement, current flow is through the interior of the overlay **5**, through the workpiece **15** because of the face to face contact with the overlay, through the milling bath and then to the ground G_2.

The preferred concentration of the sulphuric acid bath is 30% sulphuric acid by weight, although the same can be varied from 10 to 40% by weight, with a preferred range of concentration being from 20 to 30% by weight. Amperage values should be about 200 to 400 amperes. Such 200 to 400 amperes current can be defined as being in the range of from about 5 to 25 amperes/in.^{2}. Variations within such ranges will accommodate those parameters dependent upon overall time of milling, characteristics of milled piece, depth of cut desired, et cetera.

Reliance is placed upon the fact that valve metals such as aluminum and titanium, when placed in a sulphuric acid bath, become anodized upon the surfaces exposed to the bath, this causing such surfaces to be coated with aluminum or titanium oxide, as the case may be. The anodized surface is not only completely passive insofar as any acidic attack be concerned, but also renders the valve metal non-conducting at those anodized surfaces. The result is that the current in the bath is concentrated within those areas desired to be electrochemically milled, and in the embodiment of the invention herein described, within that area defined by the configuration **6** of FIG. 1.

In this arrangement, the overlay or mask **5** may be considered merely as the conductor for the electrical current, the workpiece itself comprising the anode for ionic transfer. It is apprehended that for this very reason, the two named metals have not been considered adaptable for use as anodes in any electrochemical milling procedure or procedures equivalent thereto—this simply because once exposed to acidic attack during electrolysis, the resulting and practically instantaneous anodizing of

the surface of these metals renders them completely passive insofar as current conductivity be concerned; in the instant case that problem has been resolved, and with the above-named advantages, by utilizing the mask as merely a conductor for the current to the anode (the workpiece) with the exposed portions of that conductor being not only passivated or immune to current flow, but also immune to attack by the acidic dielectric.

The metal to metal contact between workpiece and overlay effectuates such a seal that leakage therebetween is practically eliminated. Furthermore, whatever small amount of leakage that does occur is of no consequence and because of these factors: The stippled area which is designated at **36** in FIG. 4 indicates a slight discoloration or some effect of bath contact between the surfaces of overlay and workpiece, and particularly at those edges thereof which terminate together and which are exposed to the electrolyte. These areas are exaggerated simply for illustrative purposes. They represent areas which have been slightly anodized by slight leakage of the electrolyte between overlay and workpiece. The resultant chemical reaction which takes place at such points results in the formation of the oyide on the surface, as Al_2O_3 in the case of aluminum, or TiO in the case of titanium. In other words, this is the anodizing effect, resultant upon the entrapped electrolyte after the first surge of electric current. The fine layer of oxide there formed prevents any milling activity at these points; hence, such leakage presents no problem insofar as obtaining a clean and reasonably sharp milling operation at the intersecting edges of the workpiece and overlay. Stated somewhat differently, a resultant higher electrical resistance in the thin film of "leaked" and spent electrolyte plus the relatively longer electrical path from the cathode to the shielded anode limit the current density to a value which is insignificant when compared with the conditions prevailing on the front or selectively exposed side of the panel being milled.

There are, of course, two reactions which take place in each instance where either aluminum or titanium is employed as a metal for the overlay. The first of these reactions involves the anodizing of the exposed surfaces of the overlay. In electrolysis this, of course, should be represented in ionic form. The following equation typically represents the formation of the oxide (Al_2O_3) on the surface:

$$2Al + 6OH \rightarrow Al{\cdot}O_3 + 3H_2O + 6e^-$$

This anodizing or oxidation of the surface of either the aluminum or titanium takes place in the first few seconds of operation; and in that length of time such exposed surfaces become passivated for the remainder of the operation.

The second result of electrolysis is, of course, to perform the milling operation wherein the ferrous alloy is milled to the desired depth. In ionic form this removal of metal during electrolysis in the sulphuric acid bath may take the following form, and assuming the stainless steel piece be considered, for the sake of simplicity, merely as the metal iron:

$$Fe^{++} + SO_4^{=} \rightarrow FeSO_4$$

The equations for anodization of a titanium mask and metal removal by electrochemical milling when this metal be used are the same or similar.

When a preformed, permanent and reusable mask or overlay of aluminum or titanium is used, the angle of inclination of the side of the mask representing the areas to be milled, is of some significance. The edge or side here referred to is that designated by the numeral **7** in FIGS. 1 and 2. The referred to angularity is for the purpose of serving two basic functions: Firstly, such a predetermined angularity has been selected primarily to aid in the discharge of gas (oxygen) and partially spent electrolyte from the plate being milled; and, secondly, such predetermined angularity reduces the amount of possible undercutting to an extent where such undercutting (and as represented in FIG. 6) does not constitute a factor of appreciable importance. This preferred angularity may vary from between 30° to 45° to the vertical, as such side **7** is viewed, e.g., in FIG. 2. When the angularity is of lesser or greater amounts to the vertical, more than an acceptable amount of undercutting, so-called, may ensue. For practical purposes, then, the range of 30° to 45° is preferred. The following table indicates the amount of undercut which occurs at 45°, and the amount at 30°, proper interpolation varying that amount between these two angularities:

TABLE I

Surface of Steel Overlayed By Mechanical "Heavy" Mask

Angle	Depth of milling in inches	Diameter in inches of top of milled hole	Amount of undercut	Mask aperture diameter in inches
45°	.049	.475	.069	.406
30°	.055	.480	.074	.406

This amount of undercut, of course, represents, in the case of a 45° angle, the difference between .475 and .406 of an inch and with regard to a 30° angle, the difference between .475 and .406. By interpolation it can be assumed, if the angle be 37½°, the average of these two would result in .0715 inches of undercut. When depth of removal of the metal is anywhere from between about .135 to about .175 inches, as would be common in practical applications of the process, this amount of undercutting is insignificant. ,

Mention in the foregoing has been made of an alternate practice of the inventive process wherein, instead of employing a heavy, reusable overlay of aluminum or titanium, one or the other of such metals can be deposited upon the workpiece by such methods as vapor deposition, et cetera. When so deposited they take the configuration of the portion of the workpiece to be milled. In this instance, undercutting can be reduced somewhat. In one example of the invention, a piece of stainless steel was overlaid with aluminum by dipping the workpiece in molten aluminum. In an additional practice of the invention, a steel panel was painted with a silicone type aluminum bath, heated to about 750° F. to remove most of the vehicle or carrier, leaving only the aluminum overlay. Gas or vapor plating a workpiece with aluminum can also provide the overlay. The aluminum coated workpiece, however the coating may be applied, after cathodic or chemical or mechanical removal of the aluminum from the desired geometric pattern, when subsequently anodically, electrochemically exposed, showed the depth and pattern typical of the mechanical mask except that the entry edge of the cavity was somewhat sharper.

Subsequent removal of the aluminum or titanium when such is applied by the methods just referred to can be accomplished by simple chemical dissolution in either a strongly alkaline or acid solution which preferentially dissolves the aluminum. In this instance, either sodium hydroxide or potassium hydroxide are representative of strong alkalines. As an acidic solution to obtain aluminum removal, hydrofluoric acid is useful for this purpose.

In the following table, similar to Table I, the amount of undercutting is indicated where a vapor deposited, or hot metal dipped or painted overlay of aluminum has been utilized:

TABLE II

Surface of Steel Overlayed By Deposited Mask

Angle	Depth of milling in inches	Diameter in inches of top of milled hole	Amount of undercut	Mask aperture diameter in inches
45°	.052	.440	.034	.406
30°	.056	.445	.039	.406

If advantages of both systems be desired, then the mechanical mask or overlay can be used in conjunction with an undercoat of, e.g., aluminum, applied to the workpiece surface by any of the methods hereinbefore indicated. In such eventuality the amount of undercut would represent that shown in Table II, where advantage has been taken of the sharper cut due to the minimal thickness of the overlay when such systems as vapor deposition are utilized for application thereof to the workpiece surface.

It has been further found that when an applied aluminum overlay (as distinguished from the permanent mechanical preformed type) is used in the process, the overlay is still adequate to effectively conduct current at the given amperage values from an outside source to the workpiece, the anode.

Other advantages of the inventive process, particularly with regard to the method involving a permanent, reusable aluminum or titanium overlay, should be apparent to those skilled in the art.

Because made of a hard and durable metal, a preformed mask can be reused many times. When a good design is desired, it can be more easily cut into such a heavy metal base rather than into such materials as Lucite, or similar resinous materials which tend to shatter or splinter even during the most precise cutting operations. Also, the assembly of the mask with the workpiece, as a mechanical matter, is very simplified and can be done manually in a few minutes of time, this also being true of disassembly thereof after milling has been achieved. The operation itself is of relatively short duration—the cut or milled area in a piece to a depth of about one-tenth of an inch can be achieved in about 10 minutes and, of course, where multiple etchings are desired in a series of the same elements all placed in the same bath, this same period of time is involved.

As indicated in the foregoing, and whether aluminum or titanium be the selected metal as the maskant and conductor to the workpiece, the process is effective when using sulphuric acid in the concentrations heretofore given as the electrolyte. Commercially this represents a desirable feature of the process because of the relatively low cost of this inorganic acid in bulk quantities.

While the present invention has been illustrated and described in the foregoing with reference to certain particular embodiments thereof, it is not intended that it be limited to same, nor otherwise than by the terms of the claims appended hereto.

We claim:

1. For use in an electrochemical milling process for the milling of selective portions of a ferrous base metal workpiece, said workpiece being immersed in an acidic electrolyte, and electric current being passed through said workpiece and said electrolyte, said workpiece being the anode, a frame for housing and masking said workpiece, said frame comprising a self-supporting, reusable, preformed structure, said workpiece being insertable into and removable from said frame and being closely confined therein, said frame having an opening therein, the shape of said opening corresponding to the shape of said selected portion to be milled in said workpiece, and adjustable means for maintaining said workpiece in close contact with said frame at the periphery of said opening, said frame being comprised of a valve metal having characteristics such that the surface of said metal becomes anodized when immersed in an acidic electrolyte through which said current is passed, and wherein the oxide of said metal resulting from said oxidation is substantially nonconductive.

2. The invention as defined in claim 1 wherein said frame comprises first and second, spaced plate, said workpiece being confined within the space between said plates, said opening being in one of said plates.

3. The invention as defined in claim 2 wherein the periphery of said opening is beveled.

4. The invention as defined in claim 3 wherein said plates are spaced by means of shims contoured to said workpiece, said shims in combination with said plates providing close confinement for said workpiece; and means in said other plate for adjustably applying pressure to said workpiece to force said workpiece against said one plate at the periphery of said opening.

5. The invention as defined in claim 1 wherein said valve metal is aluminum.

6. The invention as defined in claim 1 wherein said valve metal is titanium.

7. The invention as defined in claim 1 wherein said frame surrounding said opening is beveled.

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U.S. Cl. X.R.

204—15, 129.65