

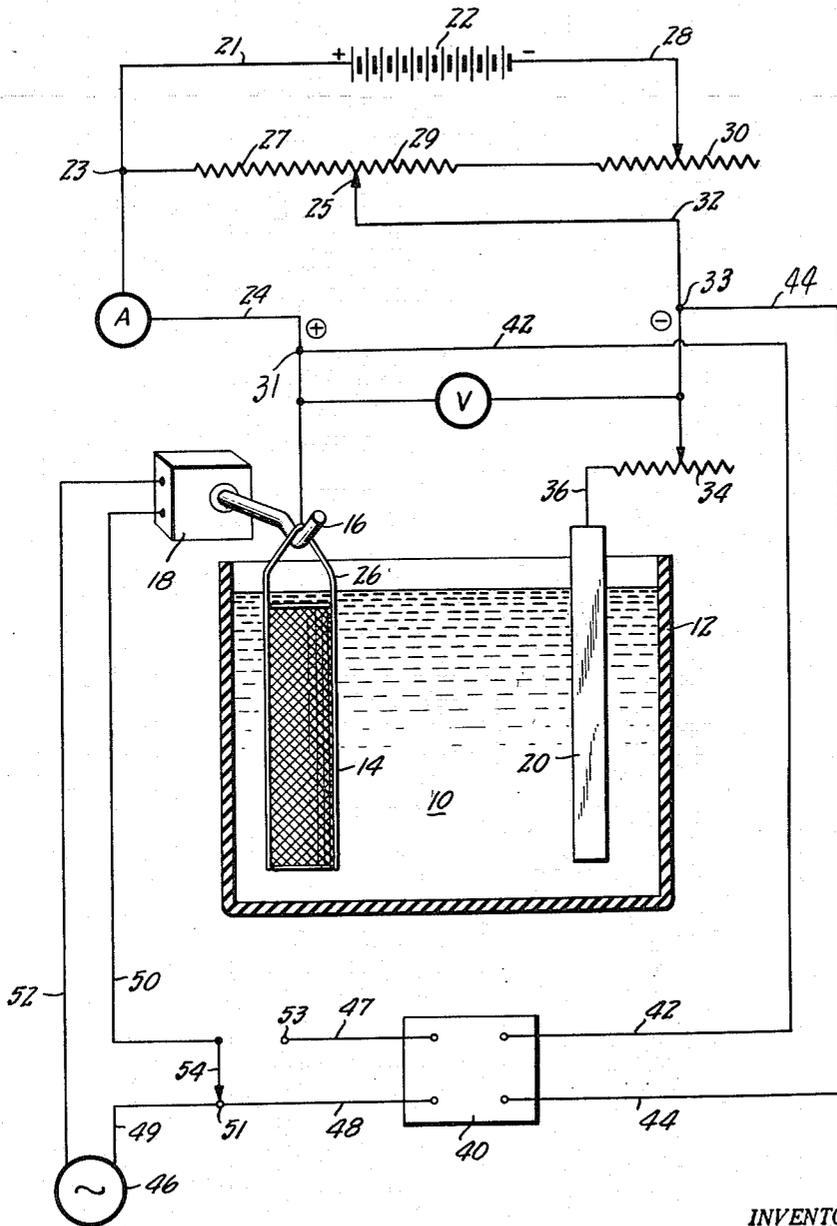
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ELECTROLYTIC DISSOLUTION OF STAINLESS STEEL

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ELECTROLYTIC DISSOLUTION OF STAINLESS STEEL

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The present invention relates to a method and apparatus for dissolving stainless steel in nitric acid.

Stainless steel usually contains chromium, nickel, iron, manganese, and other components, in varying proportions. One of the most useful and valuable properties of stainless steel having a chromium content in excess of five percent is its resistance to solution in nitric acid. However, it is sometimes desirable to dissolve stainless steel in nitric acid as for example when the steel is used as a container for materials which must be dissolved in nitric acid.

It is accordingly an object of the present invention to provide a method for solubilizing stainless steel, normally resistant to solution in nitric acid, in nitric acid.

It is another object of the present invention to provide an apparatus for dissolving stainless steel in nitric acid.

It is a further object of the present invention to provide a method for dissolving stainless steel without production of large amounts of gaseous effluents.

Other objects will be in part apparent and in part pointed out in the description of the invention which follows.

The present method involves subjecting the stainless steel to anodic attack in nitric acid solution. A number of problems arise when an attempt is made to electrolytically dissolve stainless steel.

One of the problems arises in connection with supplying current to the stainless steel specimen immersed in nitric acid. A conductive material must be employed but this material must not itself be subjected to electrolytic dissolution while supplying current to the steel since the current supplying metal itself might be dissolved before the solution of the stainless steel is complete. It has not been found practical to supply current to the stainless steel in the electrolyte through a stainless steel element which extends out of the bath because the portion of the steel specimen not immersed in the bath will not be subjected to electrolytic attack. Also the usual devices such as insulated clamps are unsatisfactory because in dissolving specimens of irregular shapes, portions of the specimens may be disconnected as the supporting portions are dissolved and thus remain undissolved.

Another problem arises when it is particularly important to prevent loss of any of the components of the stainless steel or of the contents of a stainless steel container. Thus, for example, when the stainless steel is radioactive or is employed as a container for radioactive materials, it is desirable to avoid liberation of gas at the electrodes during the electrolytic dissolution so that no radioactive contamination of the surroundings occurs. The liberation of gases at the electrodes reduces the efficiency of such an electrolytic process in any case because current must be consumed in effecting such liberation. For these reasons the use of the noble metals electrodes, such as platinum electrodes, has not been found satisfactory in carrying out the electrolytic dissolution of stainless steel since platinum liberates O₂ at 1.5

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volts and electrolytic attack of stainless steel at lower voltages is impractical.

These problems are overcome, according to one of the broader aspects of the present invention, by supplying the current through a metal which exhibits electrolytic valve action. Such a metal is one which is not subjected to electrolytic attack at lower voltages but which is subjected to such attack at higher voltages above the electrolytic valve voltage. For the purposes of this application, the voltage at which the electrolytic attack starts to take place is referred to as the valve action voltage, or electrolytic valve voltage. When such a metal is subjected to electrolytic attack in nitric acid solution, a short surge of current passes through the solution and a film is apparently developed on the surface of the metal during this short surge of current. This film is of an insulating nature since only a minute current passes through the solution after the film is formed. It has been discovered that, in spite of the presence of this insulating film on valve action metals, they may satisfactorily be employed to transmit current to a stainless steel element in the nitric acid electrolyte, but that little or no gaseous effluents are produced. It has thus been found possible to maintain an electrolytic attack on stainless steel articles in nitric acid by supplying the electrolytic current to the stainless steel through one of the metals exhibiting electrolytic valve properties. A maximum advantage is secured in dissolving articles of irregular shape by forming the metal which exhibits electrolytic valve action into a basket-like holder. A flow of electrolyzing current occurs only at the points where the stainless steel rests on the elements of the basket, the remainder of the basket remaining insulated due to the presence thereon of the insulating film. As pieces of the metal specimen become detached and fall into contact with the basket elements, electrical contact is made through the insulating coating at the point where they contact the basket to result in their electrolytic dissolution. The flow of electrolyzing current from the basket surface is thus selectively restricted to only those points where the basket is contacted by the stainless steel.

The accompanying drawing is a diagrammatic illustration, partly in section, of an electrolytic cell and the circuit diagram of an apparatus suitable for carrying out the present invention.

Although it is possible to dissolve most of the components of stainless steel, a number of these components, including columbium, columbium carbide and silicon, are not brought into solution. The release of these components, as the soluble metals are dissolved from the stainless steel, results in the deposit of an insoluble sludge between the stainless steel being subjected to electrolytic attack and the supporting metal. The deposit of this layer of sludge raises the resistance between the holder metal and stainless steel specimen and requires the voltage impressed on the holder to be raised in order to deliver the same amount of current to the stainless steel specimen. If the voltage which must be impressed to continue the electrolytic dissolution of the stainless steel exceeds the electrolytic valve action voltage, the anode metal itself is subjected to electrolytic attack by the nitric acid. This difficulty is overcome according to the present invention by providing a relative movement of the holder metal and stainless steel in order to dislodge the sludge and maintain electrolytic contact therebetween.

The advantages of the present invention may be best understood from a consideration of an illustrative embodiment of the invention which follows. It will be understood that the scope of the invention is not confined to this illustrative embodiment.

Referring to the figure, a solution of nitric acid electrolyte 10 is disposed in a container 12 composed of an

insulating material. A metal basket 14 composed of a metal exhibiting electrolytic valve action is supported in the solution from a hook 16 composed of an insulating material. This hook extends from a vibrator 18, the operation of which will be described below. A cathodic electrode 20 is also included in the electrolytic bath.

A source of direct current 22 is used to carry out the electrolytic operation. This current is supplied to the basket 14 through the electrical leads 21 and 24 and the conducting handle 26 of the basket 14. A negative potential is established on the cathode 20 by connecting the negative pole of the current source 22 with cathode 20 through the electrical lead 28, rheostat 30, the portion 29 of the potentiometer 27—29, the conductor 32, rheostat 34 and conductor 36. A voltmeter is connected between electrical leads 24 and 32 and an ammeter is connected in the electrical lead 24.

The vibrator 18 imparts a vibrating motion to the insulated hook support 16. Current is supplied to the vibrator 18 from alternating current source 46 by various conductors depending on its mode of operation. The operation of the vibrator may be made continuous so that the basket 14 is made to vibrate during the entire electrolytic operation or it may be made intermittent so that it is brought into operation only when the potential between the electrodes rises above a certain value. The positioning of a single pole, double throw switch 54 determines whether the operation is continuous or intermittent.

For continuous vibration, the switch 54 is connected to terminal 51, as shown in the figure, so that a direct connection is made between the current source 46 and the vibrator 18, through conductors 49, 50 and 52 and through switch 54.

When the vibrator is to be operated intermittently, the switch 54 is connected to the pole 53 so that a relay 40 is included in the vibrator circuit. When the switch is so connected, current is supplied to the vibrator only when the relay 40 is activated. When so activated, current flows from current source 46 through conductors 49, 48, 47, 50 and 52 and through switch 54 and relay 40 to operate vibrator 18. Relay 40 may be any conventional relay whose winding is energized at a predetermined voltage and acts to connect conductor 47 to conductor 48. The relay winding is connected across the positive terminal 31 and negative terminal 33 by means of conductors 42 and 44. Also connected between terminals 31 and 33 is the portion 27 of potentiometer 27—29. It can be seen that the resistance of the electrolyte 10 is in series with the resistance of the rheostat 34 and this series combination is similarly connected across terminals 31 and 33.

Since resistance 27 of potentiometer 27—29 and the series combination 10 and 34 are in parallel, the total resistance between terminals 23 and 25 of potentiometer 27—29 may be changed either by changing the position of the moving terminal 25 or by changing the resistance of the series combination 10 and 34. It is apparent that a change in this total resistance will result in a proportional change in the voltage appearing between terminals 23 and 25.

During the course of the electrolytic dissolution, a deposit of a sludge of the insoluble components of stainless steel forms between the surface of the basket 14 and the undissolved stainless steel. This causes an increase in the resistance of cell 10 and a corresponding rise in the voltage appearing between the terminals 23 and 25 of the potentiometer 27—29. This voltage rise is applied across the winding of relay 40 and, when the voltage reaches a predetermined value, the relay winding is energized and in turn activates the vibrator 18 by connecting conductors 47 and 48. Activation of the vibrator removes the sludge and reduces the cell resistance. This in turn reduces the voltage appearing between terminals 23 and 25 until the relay winding is de-energized and the vibra-

tor operation ceases. Thus, the vibrator is caused to operate responsive to the formation of excessive sludge between the basket and stainless steel specimen and acts to remove the sludge.

The following are examples of the method of the present invention as carried out in the illustrative apparatus described above.

Example I

A basket with a square cross section of $1\frac{1}{2}$ inches and a depth of 5 inches was welded from titanium sheet and perforated with $\frac{1}{32}$ inch holes about $\frac{1}{4}$ inch apart. The basket was filled with 100 grams of stainless steel pin tubing in 7-inch lengths and immersed in three liters of 4 molar nitric acid. The stainless steel had the following composition—about 71% iron, about 18% chromium, about 8% nickel, about 2% manganese, about 1% columbium and fractional percentages of silicon and carbon. A stainless steel strip of the same composition was used as the cathode. An electrolyzing current of 5 to 6 amperes was applied at a voltage of 3.0 to 3.1 volts employing the circuit illustrated in the figure. The relay 40 was adjusted so that the basket was vibrated whenever the cell voltage rose to about 8 volts and stopped operating when the voltage fell below 6 volts. After about three hours, the voltage was raised to 6 to 9.5 volts and the current to 20 amperes with a corresponding adjustment in the relay to accommodate this change in voltage. After a total of 10 hours operation (3 hours at the lower voltage and 7 hours at the higher), the cell was dismantled. Only a very small residue of stainless steel slivers remained undissolved. Approximately 141 ampere hours had passed during the total operation so that the current yield was about 0.71 grams per ampere hour. The loss of weight of the titanium basket was only 0.93 gram out of a total initial weight of 109.55 grams.

Example II

A cylindrical basket, $2\frac{1}{2}$ inches in diameter and 30 inches in length, was formed from tantalum sheet of 30 mil thickness. It was perforated with $\frac{1}{32}$ inch holes at approximately $\frac{1}{4}$ inch spacing. The basket was loaded with about 500 grams of stainless steel of the same composition given in Example I in the form of stainless steel pin tubing. The basket and a stainless steel strip cathode, $3\frac{1}{2}$ inches wide and 24 inches long, were immersed in 14 liters of 4 molar nitric acid. Electrolysis was begun at about 6 volts and 90 to 100 amperes. After about 6 hours, the voltage was reduced to 4 volts and the current to 70 amperes in order to avoid boiling of the solution. The vibrator was operated during the entire run so as to shake the basket in a vertical plane over a wide range of frequencies and over a range of amplitudes from 0 to $\frac{1}{4}$ inch. The charge of pin tubing was completely dissolved in the 16 hours. Evolution of gas at the cathode was almost negligible during most of the electrolysis.

Example III

Approximately 492 grams of stainless steel tubes, 30 inches in length and containing 546 grams of a '63/27 mixture of $\text{UO}_2:\text{MgO}_2$, were placed in the same basket described in Example II. The basket, together with the corresponding strip cathode, was immersed in 17 liters of 4 molar nitric acid and the basket was shaken as described in Example II. The electrolytic bath was surrounded by crushed ice so that the temperature of the electrolyte remained between 0° and 20° C. for most of the run. The initial voltage applied was 7 volts at 90 amperes. The current remained fairly constant for 7 hours but fluctuated after this until the dissolution of the assembly was completed at the end of $8\frac{3}{4}$ hours. The solution was then heated to about 90° C. for 4 hours in order to complete the dissolution of UO_2 . After this solution was centrifuged in order to recover and

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wash the residual sludge of insoluble components. Upon analysis, the sludge was found to contain only 0.05% of the uranium originally present in the assembly. Approximately 709.3 ampere hours passed during the electrolytic dissolution corresponding to an anodic dissolution yield of 0.69 grams of stainless steel per ampere hour. Gas evolution from the cathode was again relatively small in amount.

From the foregoing, it is apparent that the present invention provides a novel and useful method for dissolving stainless steel, normally insoluble in nitric acid, in nitric acid. It is further apparent that the electrolytic dissolution can be carried out according to the present invention using relatively low voltages below the electrolytic valve voltage of the metal basket used to transmit current to the stainless steel.

Metals suitable for this purpose must of course be insoluble in nitric acid and must exhibit an electrolytic valve action. Among such metals are columbium, tantalum, titanium and zirconium. Tantalum remains passive up to 120 volts in 4 molar nitric acid, titanium is similarly passive up to 12 volts and zirconium up to 90 volts.

To dissolve stainless steel electrolytically, a minimum voltage of 1.3 volts must be applied and the maximum voltage is that just below the valve action voltage for each valve action metal.

Although 4 molar nitric acid has been found most economical in carrying out the present process, either more or less concentrated acid may be used.

Since many embodiments might be made of the present invention and since many changes might be made in the embodiment described, it is to be understood that the foregoing description is to be interpreted as illustrative only and not in a limiting sense.

I claim:

1. Apparatus for substantially completely dissolving radioactive stainless steel elements in nitric acid, the steel of said elements having a high chromium content, said

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apparatus comprising an electrolytic cell adapted to contain nitric acid, a source of electrolyzing current, means for supplying said electrolyzing current to said elements in said bath, said means comprising a cathode and an anode holder in said cell, said anode holder being composed entirely of a metal selected from the group consisting of tantalum, columbium, titanium and zirconium, said anode holder being adapted to receive and support said stainless steel elements and being coated with a film formed by subjecting said metal to electrolytic attack in nitric acid whereby said holder is adapted to supply electrolyzing current to said steel elements in nitric acid bath only at points where said elements rest in contact with said anode holder and means for agitating said holder.

2. The apparatus of claim 1 in which the selected metal is tantalum.

3. The apparatus of claim 1, in which the selected metal is titanium.

4. The apparatus of claim 1 in which the selected metal is zirconium.

5. The apparatus of claim 1 in which the selected metal is columbium.

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