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3,088,889
ELECTROLYTIC MACHINING OF METAL SURFACES
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This invention relates to the shaping of metal parts and more particularly to a bath solution and process for shaping metal parts by controlled electrolytic dissolution.

In recent years it has increasingly become more apparent that conventional methods of machining parts, particularly aircraft parts, have become inadequate for obtaining present day needs. Various methods of fabricating aircraft parts have been employed in the past to obtain high strength, exceedingly lightweight articles. However, the conventional methods still do not readily permit the manufacture of parts having the most desirable strength-to-weight ratios. Moreover, many of the metals currently being employed because of high strength and corrosion resistance at elevated temperatures are exceptionally hard and, therefore, difficult to conventionally machine. Conventional machining operations, such as milling, grinding, etc. are accomplished very slowly with these relatively hard materials and, accordingly, machining such materials to the degree required to obtain optimum strength-to-weight ratios is expensive and tedious.

In the manufacture of hollow turbine buckets for a jet engine, for example, corrosion-resistant, extremely hard alloys of nickel or cobalt are frequently used. These turbine buckets need only have exceedingly thin walls for strength purposes and such thin walls are especially desired for efficient cooling of the blades. Moreover, the outer surface of the turbine bucket should be as smooth as possible to reduce friction with gaseous streams passing over the bucket. The fabrication of such a turbine bucket by conventional techniques is exceedingly difficult, time consuming and costly.

Alloys, such as nickel and cobalt base alloys referred to above typically are formed by casting, molding or the like. Some high temperature alloys, such as stainless steel, may also be forged. An undesirable projection frequently results at the parting line of the forming members. Similarly, during conventional machining operations a burr is likely to result on the periphery of the machined surface. These undesirable projections on the surface of the part must subsequently be removed by finishing operations. However, such finish operations are additionally time consuming and costly.

It is a primary object of this invention to provide a bath solution and process for electrolytically treating a metal surface in such a manner as to dissolve the metal of the surface at a rapid rate while concurrently maintaining or improving the smoothness of the surface.

It is universally recognized that the surface finish of a part which is subjected to physical and thermal stresses should be exceptionally smooth. It is expected that the extremely smooth surface finishes are not only desirable when the part is to be used in a gas stream but, in most instances, necessary to obtain optimum resistance to fatigue and corrosion. Our invention provides a means whereby the surface of a part made of metals, such as stainless

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steels, nickel base alloys or cobalt base alloys, is subjected to a controlled etching which can be used to improve the smoothness or surface finish of the part to remove undesirable surface projections and to produce exceedingly thin structures.

Accordingly, it is a further object of our invention to provide a means whereby such materials can be produced economically and rapidly under commercial production conditions to produce optimum strength-to-weight ratios heretofore frequently unobtainable and to concurrently obtain surface finishes which were only laboriously obtained by conventional finishing techniques.

We have now found that a stainless steel alloy, a nickel base alloy or a cobalt base alloy can be satisfactorily machined by electrolytic dissolution in an acid aqueous bath containing ammonium ions, fluoride ions and cupric ions. By "surface finish," as used herein, we refer to the degree of smoothness or roughness of a given surface as distinguished from the degree or reflectivity of a polished surface.

By the term "controlled etching," as used herein, we refer to the etching of a metal surface in such a manner as to uniformly dissolve the metal without selectively etching grain boundaries or grain of the metal, thus at least maintaining the original surface condition. Such controlled etching will concurrently attack projections or peaks on the surface to a greater degree than recesses or valleys, thereby concurrently smoothing out or leveling the surface.

Our invention is generally satisfactory for rapidly and economically dissolving metals, such as stainless steels, nickel base alloys and cobalt base alloys. For the purposes of our invention by the term "stainless steel" we intend to encompass various ferrous base alloys containing approximately 10% or more chromium, such as alloys analogous to the SAE 300 and SAE 400 series stainless steels. More specifically, this invention is effective in the controlled etching of metals given as examples in the following Table I, the compositions being listed in percent, by weight:

Table I

	Example 1	Example 2	Example 3
Carbon.....	0.08	0.15 Max.	0.08-1.12
Manganese.....	-----	1.0 Max.	0.75-1.25
Silicon.....	-----	1.0 Max.	0.5 Max.
Phosphorus.....	-----	0.04 Max.	0.04 Max.
Sulfur.....	-----	0.03 Max.	0.03 Max.
Chromium.....	14.55	11.5-13.5	16.00-17.00
Nickel.....	25.00	0.75 Max.	4.0-5.0
Molybdenum.....	1.25	0.5 Max.	2.5-3.25
Aluminum.....	0.2	0.05 Max.	-----
Sodium.....	2.5	-----	-----
Titanium.....	1.9	-----	-----
Copper.....	-----	0.5 Max.	-----
Tin.....	-----	0.05 Max.	-----
Nitrogen.....	-----	-----	0.07-0.13
Iron.....	Balance	Balance	Balance

Although stainless steels can be treated in accordance with our invention, greater advantages are realized in the treatment of nickel base and cobalt base alloys. References made herein to nickel base alloys and cobalt base alloys are intended to include those metals, respectively, containing more than 50%, by weight, nickel and more than 50%, by weight, cobalt.

The following Table II contains examples of suitable

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high temperature, creep-resistant nickel base alloys which may be satisfactorily electrolytically machined in accordance with the present invention, the compositions being listed in percent, by weight:

Table II

	Example 1	Example 2	Example 3	Example 4	Example 5
Carbon	0.15 Max.	0.35-0.45	0.07 Max.	0.15	0.08 Max.
Manganese	1 Max.	2-3	1 Max.	1 Max.	0.3-1
Chromium	15.5-17.5	23.5-26.5	19.5	19	14-16
Cobalt	2.5 Max.	10-15	13.5	10	
Molybdenum	16-18	2-4	4.25	10	
Tungsten	3.75-5.25	6-8			
Iron	4.5-7	5 Max.	2 Max.	5 Max.	5-9
Vanadium	0.2-0.6				
Titanium			2.5	2.5	2.25-2.75
Aluminum			1.25	0.87	0.4-1
Silicon	1 Max.	1 Max.	0.75 Max.	0.65 Max.	0.5 Max.
Sulfur		0.03 Max.			0.01 Max.
Copper					0.2 Max.
Nickel	Balance	Balance	Balance	Balance	Balance

However, the nickel base alloy disclosed in United States Patent No. 2,688,536, Webber et al., appears to be one of the most outstanding turbine bucket materials currently available with respect to stress-rupture properties, creep resistance, ductility and high temperature corrosion resistance. This alloy comprises approximately 0.06% to 0.25% carbon, 13% to 17% chromium, 4% to 6% molybdenum, 8% to 12% iron, 1.5% to 3% titanium, 1% to 4% aluminum, 0.01% to 0.5% boron and the balance substantially all nickel. For some applications the aluminum content may be increased to approximately 6% and the iron content may be as low as 0.1% or as high as 35%. The alloy usually should not contain more than 20% iron, however. Normally, manganese and silicon not in excess of 1% each are also included in the alloy.

Examples of high temperature cobalt base alloys which may be machined with controlled etching in accordance with our invention are listed in the following Table III, the composition again being given in percent, by weight:

Table III

	Example 1	Example 2	Example 3	Example 4
Carbon	0.20-0.35	0.45-0.60	0.20 Max.	0.32-0.4
Manganese			1.00-2.00	0.60-1.80
Silicon			0.60 Max.	0.30-0.90
Sulfur			0.04 Max.	
Chromium	25.00-30.00	23.00-28.00	20.00-22.00	19.00-21.00
Nickel	1.50-3.50	9.00-12.00	18.00-22.00	19.00-21.00
Molybdenum	4.50-6.50		2.50-3.25	3.50-4.50
Tungsten		6.00-9.00	2.00-3.00	3.50-5.00
Columbium			0.75-1.25	3.00-4.50
Nitrogen			0.08-0.16	
Iron	2.00 Max.	2.00 Max.		5.00 Max.
Cobalt	Balance	Balance	18.00-22.00	40.00-44.00

As previously described, the bath of our invention encompasses an acid aqueous solution containing ammonium ions, fluoride ions and cupric ions. The ammonium ions, fluoride ions and acidifying hydrogen ions preferably are introduced into the solution in the relative stoichiometric proportions of 1:1:2, respectively. It has been found that generally satisfactory results are obtained when the ion concentrations are maintained at a value corresponding to that produced by dissolving approximately 20 grams to 200 grams ammonium bifluoride in 1,000 milliliters of water. The fluoride ions may be introduced in the form of hydrofluoric acid which simultaneously acidifies the solution. It is contemplated that there are a number of soluble fluoride salts, such as ammonium fluoride and ammonium bifluoride which may advantageously be used to supply the fluoride ion to avoid handling of the highly corrosive acid. Accordingly, the desired fluoride and hydrogen ion concentrations can be obtained in a number of ways using the suitable ion-contributing compounds.

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A part or all of the preferred ammonium ion content of the solution, as indicated above, may be supplied in conjunction with the fluoride ion-contributing salt. However, the ammonium ions can also be introduced into the solution as ammonium hydroxide. By using hydrofluoric acid as the fluoride ion-contributing substance, proper relative additions can be made to provide the desired concentration and relative stoichiometric proportions of the ammonium, fluoride and hydrogen ions. When the desired ammonium ion concentration in the bath is attained by using ammonium fluoride, the preferred relative amount of fluoride ions and hydrogen ions can be introduced by some other compound, such as hydrofluoric acid. Thus, all of the ammonium ions or the balance required may be introduced in the form of any suitable ammonium compound.

Satisfactory results can be obtained using a soluble copper salt, such as a cupric sulfate in the solution in quantities of from about 40 grams per liter to 400 grams per liter. However, generally satisfactory results can be obtained using any suitable cupric ion-contributing salt in such a concentration as to produce a cupric ion concentration of approximately 10 grams per liter to 105 grams per liter. It is also contemplated that a number of suitable cupric ion-containing salts, such as cupric nitrate, can be used in addition to cupric sulfate. Although the concentrations of the various bath constituents can be varied to some extent, most effective results have been obtained using a cupric ion concentration generally about 75% to 85%, by weight, of the fluoride ion concentration.

When using a bath of our composition to form metal parts by electrical dissolution techniques, the part preferably is initially cast, forged or premachined to a preform configuration of desired measurements prior to the electrical dissolution treatment. It is generally desirable to form the part slightly oversize when no masking is employed so that during the electrolytic dissolution thereof the part is reduced to finish dimensions. It is preferred, however, to form the part only as close to final desired specifications as is practical and economical by conventional techniques, keeping in mind that electrolytic dissolution tends to promote dimensional loss at high current density areas. The optimum configuration of the preformed part is dependent upon the general structure of the part involved, the practicality of using extended amounts of conventional machining techniques prior to electrical machining, etc.

It is generally preferred to clean the metal surface prior to subjecting it to electrical dissolution treatments. Satisfactory results are obtainable when the part is cleaned by degreasing it in a trichloroethylene vapor at a temperature of approximately 180° F. in the normal and accepted manner. In some instances one of the many commercially available di-phase cleaners, which is a stable emulsion of an organic cleaner and an alkali cleaner, might be used.

After degreasing, the part is dried and then, suitably supported, immersed in the electrical machining bath and attached to a source of positive potential. In general we prefer to employ stainless steel cathodes when practicing our invention but any other suitable material can be used, provided that it is sufficiently conductive and has a low cathode reaction with the bath.

The part is preferably positioned in the machining solution in such a manner as to avoid non-uniform dissolution of the surfaces. Gas which may be generated during the dissolution of the metal part can accumulate in recesses of horizontal areas of the part so as to interfere with uniform chemical dissolution of the entire surface. When electrically machining an article having a planar configuration, such as a panel, it is desirable to support the panel in the machining solution in a vertical attitude.

On the other hand, articles of a more complicated con-

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figuration containing complex contours and recesses may not be suitably maintained in any position which will entirely inhibit collection of the generated gases and formation of gas pockets. For these and other types of articles it may be desirable to chemically machine the parts in a plurality of steps in which portions of the part are masked from the solution. For example, the top of such an article can be chemically machined while its lower surface is masked with a suitable stop-off material. When sufficient metal removal of the upper surface is obtained, the part is removed from the solution, rinsed and the stop-off removed to expose the protected surface. The machined surface is then masked and the part reimmersed for completion of the chemical machining of the part. Of course, on reimmersion the part is inverted as compared to the previous machining operation so that the masked surface is on the bottom of the part. Once immersed in the solution the part is subjected to a positive potential sufficient to produce a suitable current density on the part.

The current densities which are employed generally are quite high and significant benefits of our invention can be obtained by using a current density above about 750 amperes per square foot. However, much higher current densities are preferred since highly satisfactory metal removal rates are obtained along with a high degree of surface leveling at the higher current densities. Current densities of approximately 1,500 amperes per square foot to 3,000 amperes per square foot have been used. In some instances, it may be preferred to employ current densities as high as 5,000 amperes per square foot, but in so doing especially effective cooling of the bath solution must be used. The passage of the high density current effects a heating of the bath solution. This heating must be compensated by suitable means for cooling the bath during operation. When the extremely high current densities are employed the means of cooling must be especially effective to inhibit boiling and volatilization of the bath.

The temperature at which the bath is operated is not especially critical and, in some instances, temperatures as low as room temperature can be used. Relatively high bath temperatures are preferred for commercial production use in order to reduce the resistance of the solution and pass more current through the solution per unit voltage. Accordingly, we have found that bath temperatures above 175° F. are most desirable with the upper temperature limit, of course, being somewhat below the boiling point of the solution to avoid excessive vaporization.

More specifically, a bath which is extremely satisfactory for rapidly electrolytically machining and leveling the surface of a part made of GMR 235 was made up as follows:

Ammonium bifluoride	-----g--	100
Cupric nitrate trihydrate	-----g--	200
Water	-----ml--	650

The part was subjected to an anodic potential of approximately 10 volts to 12 volts at a bath temperature of approximately 80° F. to 140° F. using a stainless steel cathode. Under the above-described conditions a current density of approximately 1,500 amperes per square foot was obtained.

Another example of a solution useful for machining GMR 235, GMR 235-D, GMR 236 and Haynes-Stellite HS-31 type alloys is as follows:

Ammonium bifluoride	-----g--	50
Cupric sulfate pentahydrate	-----g--	100
Water	-----ml--	750

The bath was operated at a temperature of 120° F. using a stainless steel cathode. The part was subjected to an anodic potential of approximately 12.5 volts to induce a current density of approximately 1,500 amperes per square foot on the part.

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The duration of the machining operation is primarily dependent upon the desired depth to which one desires to etch. In determining the preferred duration of etching one must give consideration, of course, to the fact that high current density areas on the part tend to dissolve at a greater rate than lower current density areas contributing to dimensional loss. Dissolution durations limited by such dimensional loss can be extended by initially forming the part to compensate for faster metal removal in the high current density areas. Analogously, dimensional loss can be inhibited by using maskants and bleeders in high current density areas, such as are well known in the electrical etching art.

Although this invention has been described in connection with certain specific examples thereof, no limitation is intended thereby except as defined in the appended claims.

We claim:

1. The method of electrolytically machining a metal from the class consisting of stainless steel, nickel base alloy and cobalt base alloys, said method comprising making the metal an anode in an aqueous solution consisting essentially of water, ammonium ions, fluoride ions and hydrogen ions, said ammonium, fluoride and hydrogen ions being in the respective concentrations generally corresponding to that produced by dissolving about 20-200 grams ammonium bifluoride in one liter of water, providing a suitable cathode and passing electrical current through the resulting cell so as to induce on said metal an anodic current density of at least about 750 amperes per square foot.

2. The method of electrolytically machining a metal from the class consisting of stainless steel, nickel base alloy and cobalt base alloy, said method comprising making the metal an anode in an aqueous solution consisting essentially of, in addition to water, ammonium ions, fluoride ions, hydrogen ions, said ions being in respective concentrations generally corresponding to that produced by dissolving 20-200 grams ammonium bifluoride in one liter of water, and a suitable cupric ion-contributing salt in an amount sufficient to yield about 10 grams per liter to 105 grams per liter of cupric ion, providing a suitable cathode and passing electrical current through the resulting cell to induce on said metal an anodic current density of about 750-5000 amperes per square foot.

3. The method of electrolytically machining a metal consisting essentially of, by weight, about 0.06-0.25% carbon, 13-17% chromium, 4-6% molybdenum, 1-6% aluminum, 1.5-3% titanium, iron not in excess of 20% and boron not in excess of 0.5% and the balance substantially all nickel, said method comprising making the metal an anode in an aqueous bath consisting essentially of 10-105 grams per liter of cupric ion, ammonium ions, fluoride ions, hydrogen ions and water, said ammonium, fluoride and hydrogen ions being in the respective concentrations generally corresponding to that produced by dissolving about 20-200 grams ammonium bifluoride in one liter of water, providing a suitable cathode and passing electrical current through the resulting cell so as to induce on said metal a current density of at least about 750 amperes per square foot to thereby dissolve said metal at a rate of at least about 0.003 inch per minute while concurrently at least maintaining surface smoothness.

4. The method of electrolytically machining a metal from the class consisting of stainless steel, nickel base alloy and cobalt base alloy, said method comprising making the metal an anode in an aqueous solution consisting essentially of ammonium ions, fluoride ions, hydrogen ions and cupric ions, said ammonium, fluoride and hydrogen ions being in the respective concentrations generally corresponding to that produced by dissolving about 20-200 grams ammonium bifluoride in one liter of water, the pH of said solution being below about 7 and the

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cupric ion concentration being generally about 75-85%, by weight, of the fluoride ion concentration, providing a suitable cathode and passing electrical current through the resulting cell so as to induce on said metal an anodic current density of at least about 750 amperes per square foot to thereby dissolve said metal at a rate of at least approximately 0.003 inch per minute while concurrently at least maintaining surface smoothness.

5. The method of electrolytically machining a metal from the class consisting of stainless steel, nickel base alloy and cobalt base alloy, said method comprising making the metal an anode in an aqueous solution consisting essentially of water, the equivalent of about 20-200 grams ammonium bifluoride per liter of water and at least one cupric salt from the class consisting of cupric nitrate and cupric sulfate, the concentration of cupric salt being approximately twice that of said ammonium bifluoride, providing a suitable cathode and passing elec-

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trical current through the resulting cell to induce on said metal an anodic current density of about 750-5000 amperes per square foot.

References Cited in the file of this patent

UNITED STATES PATENTS

2,457,060	McQuire	Dec. 21, 1948
2,625,468	Prance	Jan. 13, 1953
2,719,781	Hesch	Oct. 4, 1955
2,742,416	Jenny	Apr. 17, 1956
2,766,199	Higgins	Oct. 9, 1956
2,904,479	McCord	Sept. 15, 1959

FOREIGN PATENTS

28,319	Great Britain	Dec. 12, 1907
294,237	Great Britain	Sept. 12, 1929
530,041	Great Britain	Dec. 4, 1940
556,797	Great Britain	Oct. 21, 1943