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TREATMENT 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 chemical 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 air 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.

Parts made from metals, such as stainless steel, nickel and cobalt base alloys referred to above, frequently are formed by casting, molding or the like wherein 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 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 steels, nickel base alloys and particularly 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 cobalt base alloy can be satisfactorily machined by chemical dissolution in an aqueous bath containing ferric chloride, hydrochloric acid, hydrofluoric acid, nitric acid and iodine. By "surface finish," as used herein, we refer to the degree of smoothness or roughness of a given surface as distinguished from the degree of 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.

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. 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.

Many stainless steels and nickel base alloys may be chemically machined with the bath composition of our invention. However, far greater advantages are realized in the treatment of cobalt base alloys.

The following Table I contains examples of suitable high temperature cobalt base alloys which may be satisfactorily chemically machined in accordance with the present invention, the compositions being listed in percent, by weight:

Table I

	Example 1	Example 2	Example 3
Carbon	0.20–0.35	[1] 0.20	0.32–0.42
Manganese		1.00–2.00	0.60–1.80
Silicon		[1] 0.60	0.30–0.90
Sulfur		[1] 0.40	
Chromium	25.00–30.00	20.00–22.00	19.00–21.00
Nickel	1.50–3.50	18.00–22.00	19.00–21.00
Molybdenum	4.50–6.50	2.50–3.25	3.50–4.50
Tungsten		2.00–3.00	3.50–5.00
Columbium		0.75–1.25	3.00–4.50
Nitrogen		0.08–0.16	
Iron	[1] 2.00		[1] 5.00
Cobalt	[2]	18.00–22.00	40.00–44.00

[1] Max.
[2] Balance.

We have also found that the alloys listed in the following Table II, the compositions of which are listed in percent, by weight, are so resistant to uniform chemical attack that they cannot be satisfactorily chemically etched without the use of our invention:

Table II

	Example 1	Example 2
Carbon	0.45–0.60	0.12
Chromium	23.00–28.00	20.00
Tungsten	6.00–9.00	14.00
Nickel	9.12	10.00
Iron	[1] 2.00	[1] 2.00
Cobalt	[2]	[2]

[1] Max.
[2] Balance.

As previously indicated the bath of our invention en-

compasses an aqueous solution containing ferric chloride, hydrochloric acid, nitric acid, hydrofluoric acid and iodine. The ferric chloride used in the bath can be added as a solid or in aqueous solution. We prefer to employ a commercially available, comparatively lower cost aqueous ferric chloride solution having a density of a 42° Baumé (about 546 grams per liter). When chemically machining an alloy, such as described in Table II, we prefer to employ about 400 milliliters of a 42° Baumé ferric chloride solution (about 219 grams of ferric chloride) in every 900 milliliters of bath solution. Thus, for these alloys we prefer to employ a bath solution containing the equivalent of about 44%, by volume, of a 42° Baumé ferric chloride solution. In general, however, satisfactory results can be obtained if the ferric chloride is maintained in amounts produced by additions of about 360 milliliters to 440 milliliters in every 900 milliliters of bath solution. In certain instances, it may be preferred to use as low as about 35% or as high as about 55%, by volume, of the 42° Baumé solution in the bath solution.

Similarly, the amount of hydrochloric acid in our solution is somewhat variable. However, for alloys, such as listed in Table II, we prefer to employ about 300 milliliters, about 33%, by volume, of concentrated hydrochloric acid (specific gravity 1.19) in forming every 900 milliliters of bath solution. Generally, satisfactory results can be obtained with our bath solution when the bath solution contains about 26% to 40% of concentrated hydrochloric acid.

The nitric acid content in about 900 milliliters of bath solution is preferably equivalent to approximately 100 milliliters of concentrated nitric acid (specific gravity 1.42). In certain instances, we may prefer to employ a bath solution containing as low as about 8% or as high as about 14%, by volume, of concentrated nitric acid.

Of course, the amount of water used in forming the bath solution will vary according to the proportions of other materials which are used in forming the bath. Since it is preferred to add concentrated acid to water rather than vice versa, we prefer to add sufficient amounts of other bath ingredients to a given volume of water to obtain the desired bath proportions.

Some cobalt base alloys have a tendency to be extremely non-reactive to highly corrosive acids, such as those used in our bath solution. An alloy of the type described in Example 1 of Table II is virtually non-reactive to the bath solution unless iodine crystals are added to the bath. The amount of iodine which is employed is variable, but the rate of the reaction with this alloy as well as many others primarily depends upon the amount of reactive iodine which is present in the solution. Even small amounts of iodine present in the solution are effective in making such a metal reactive to the solution although higher amounts of about 5 grams are preferred to accelerate the reaction of the solution with the alloy. Amounts of crystalline iodine in excess of 5 grams do not appear to dissolve in the solution and, accordingly, do not appear to provide any material advantages. In general, for maximum reactivity, we prefer to employ about 5 grams of crystalline iodine in every 900 milliliters of bath solution.

It has been found that occasionally an especially non-reactive metal, such as the cobalt alloys listed in Table III, will passivate after a period of reaction with our solution. In such instance, it is necessary to remove the part from the bath solution, rinse in cold water, vapor blast the surface of the metal and then dip the part in hydrochloric acid, preferably concentrated, for a few seconds. The part can then be reimmersed in the bath solution whereupon further reaction with the solution will occur. The specific character of the vapor blast is only as critical to preserving the finish as in any other treatment involving a vapor blast and can be accomplished in the known and accepted manner.

In the vapor blast treatment the length of time that the vapor-liquid-abrasive stream should be applied depends upon the hardness of the particular metal being treated. Periods in excess of about one minute to two minutes usually should be avoided. An abrasive liquid slurry containing one volume of an abrasive of about 325 mesh to 3 volumes of liquid can be aspirated into a vapor stream having a pressure of at least about 40 pounds per square inch. Any suitable liquid can be used, such as water or a volatile organic solvent.

If excessive amounts of metal removal are desired, passivation of the metal part may occur during the prolonged duration of removal. Accordingly, activation in the above-described manner may be repeatedly necessary in order to complete metal removal to the desired depth. Alloys, such as the examples in Table I or Table II need not be activated in most instances.

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 chemical machining 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 chemically 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 configuration 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.

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 accelerate the reaction of the metal with the solution and, accordingly, are desired. Accordingly, we have found that bath temperatures above about 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.

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 projections on a part tend to dissolve at a greater rate than recessed areas contributing to a dimensional loss. Dissolution durations limited by such dimensional loss can be extended by initially forming the part to compensate for faster metal removal in areas of a projec-

tion. Analogously, dimensional loss can be inhibited by using maskants and the like, such as are well known in the 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. An aqueous bath for the chemical controlled etching of a metal from the group consisting of stainless steel, nickel base alloys and cobalt base alloys, said bath consisting essentially of the equivalent of about 35% to 55% of a 42° Baumé aqueous ferric chloride solution, about 26% to 40% of concentrated hydrochloric acid and about 8% to 14% of concentrated nitric acid, all proportions by volume.

2. An aqueous bath for the chemical controlled etching of the surface of a metal from the group consisting of stainless steel, nickel base alloys and cobalt base alloys, said bath consisting essentially of approximately 35% to 55% of a 42° Baumé aqueous ferric chloride solution, about 26% to 40% of concentrated hydrochloric acid, about 8% to 14% of concentrated nitric acid, all proportions by volume, and sufficient iodine to at least substantially maintain surface smoothness.

3. An aqueous bath for the chemical controlled etching of the surface of a metal comprising, by weight, about 20% to 30% chromium, 2% to 14% tungsten, 1% to 21% nickel, 0.6% maximum carbon, 5% maximum iron and the balance cobalt, said bath consisting essentially of approximately 35% to 55% of a 42° Baumé aqueous ferric chloride solution, about 26% to 40% of concentrated hydrochloric acid, about 8% to 14% of concentrated nitric acid, all proportions by volume, and sufficient iodine to at least substantially maintain surface smoothness.

4. The method of chemically machining a part made of a metal from the group consisting of stainless steel, nickel base alloys and cobalt base alloys, said method comprising applying to said part an aqueous bath solution consisting essentially of approximately 35% to 55% of a 42° Baumé aqueous ferric chloride solution, about 26% to 40% of concentrated hydrochloric acid, about 8% to 14% of concentrated nitric acid, all proportions by volume, and sufficient iodine to at least substantially maintain surface smoothness.

5. The method of chemically machining a cobalt base alloy part which comprises applying to said part an aqueous bath solution consisting essentially of approximately 35% to 55% of a 42° Baumé aqueous ferric chloride solution, about 26% to 40% of concentrated hydrochloric acid, about 8% to 14% of concentrated nitric acid, all proportions by volume, and sufficient iodine to at least substantially maintain surface smoothness and etching said surface to a depth of about 0.003 inch per minute while simultaneously at least substantially maintaining surface smoothness.

6. The method of chemically machining a cobalt base alloy part which comprises applying to said part an aqueous bath solution consisting essentially of approximately 35% to 55% of a 42° Baumé aqueous ferric chloride solution, about 26% to 40% of concentrated hydrochloric acid, about 8% to 14% of concentrated nitric acid, all proportions by volume, and sufficient iodine to at least substantially maintain surface smoothness, subsequently vapor blasting said surface, applying to said surface a concentrated hydrochloric acid solution and subsequently reapplying said bath solution to said surface.

7. The method of chemically machining a part made of a metal comprising, by weight, about 20% to 30% chromium, 2% to 14% tungsten, 1% to 21% nickel, 0.6% maximum carbon, 5% maximum iron and the balance cobalt, said method comprising applying to said part an aqueous bath solution consisting essentially of approximately 35% to 55% of a 42° Baumé aqueous ferric chloride solution, about 26% to 40% of concentrated hydrochloric acid, about 8% to 14% of concentrated nitric acid, all proportions by volume, and sufficient iodine to at least substantially maintain surface smoothness.

8. The method of chemically machining a part made of a metal comprising, by weight, about 23% to 28% chromium, 6% to 9% tungsten, 9% nickel, 0.45% to 0.60% carbon, 2% maximum iron and the balance cobalt, said method comprising applying to said part an aqueous bath solution consisting essentially of approximately 35% to 55% of a 42° Baumé aqueous ferric chloride solution, about 26% to 40% of concentrated hydrochloric acid, about 8% to 14% of concentrated nitric acid, all proportions by volume, and sufficient iodine to at least substantialy maintain surface smoothness, subsequently vapor blasting said surface, applying to said surface a concentrated hydrochloric acid solution and subsequently reapplying said bath solution to said surface.

9. The method of chemically machining a cobalt base alloy part which comprises applying to a surface of said part an aqueous bath solution consisting essentially of approximately 35% to 55% of a 42° Baumé aqueous ferric chloride solution, about 26% to 40% of concentrated hydrochloric acid, about 8% to 14% of concentrated nitric acid, all proportions by volume, and sufficient iodine to at least substantially maintain surface smoothness, etching said surface to a depth of about 0.003 inch per minute while simultaneously at least substantially maintaining surface smoothness, thereafter vapor blasting said surface, applying to said surface a concentrated hydrochloric acid solution and subsequently reapplying said bath solution to said surface.

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