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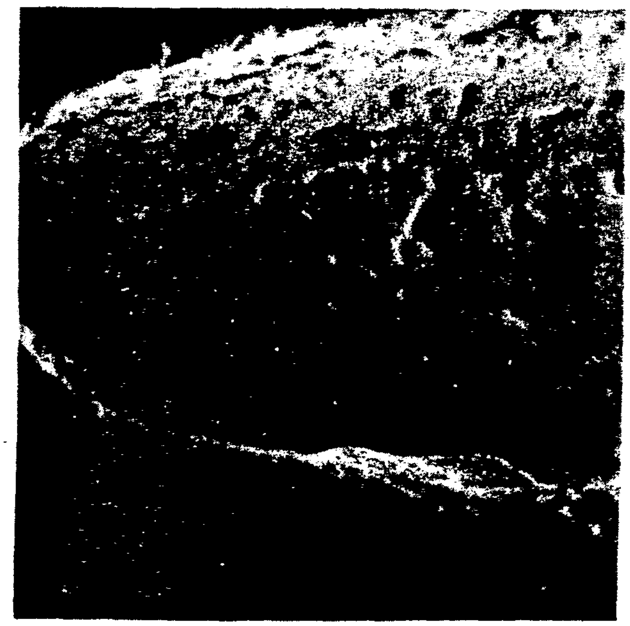
(54) **Etchant and process for machining the surface of a nickel base superalloy workpiece.**

(57) Disclosed is a process for machining nickel-base superalloys wherein a thermal-effect process, such as laser or electric discharge machining, is first used to remove material but leaves a recast layer. Next a chemical milling process is used wherein the etchant only attacks and removes the recast layer. The etchant is comprised by volume percent of 40–60 HNO_3, 5–20 HCl, and 20–55 H_2O, with which is included 0.016–0.025 moles/liter $FeCl_3$ and at least 0.008 moles/liter $CuSO_4$. The $FeCl_3$ improves removal rate but tends to cause unwanted pitting and intergranular attack. These tendencies are inhibited by the addition of $CuSO_4$; preferably the molar ratio of $CuSO_4$ to $FeCl_3$ is 2:1. The beneficial combination of $FeCl_3$ and $CuSO_4$ is usable in other etchants.



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Etchant and process for machining the surface of a nickel base superalloy workpiece

The present invention relates to an etchant and process for machining the surface of a nickel base superalloy workpiece.

The machining of the superalloys is carried out by chemical milling in combination with thermal effect metal removal processes, such as those utilizing electric discharge and lasers.

As a class of materials, superalloys used in the manufacture of airfoils for gas turbine engines are quite difficult to machine by conventional metal cutting processes using tool bits and the like which convert metal into small chips. Two types of machining are particularly difficult: drilling fine holes through the walls of hollow airfoils, and providing a complex contoured three-dimensional surface shape, such as a pattern of grooves. As a result many innovative processes have been developed in the last few decades, including those utilizing steady and intermittent electric discharge, lasers, electron beams, electrochemistry and chemical attack.

However, many of these advanced processes have their disadvantages. As a class, the electrochemical and chemical processes suffer from a lack of precision, at least to the high tolerance required in many gas turbine engine components. Also most cast and wrought airfoil materials have some metallurgical inhomogeneities and a multiplicity of phases with different compositions. Resultant local variations in resistance to the chemical attack often can lead to undesirable irregular surface finishes, or in the worst case, preferential and excessive attack of certain areas such as grain boundaries resulting in an unusable fatigue crack prone surface. Consequently , the selection of etchants and electrolytes must be carefully considered and controlled, especially in chemical milling where the inherent corrosion resistance of the superalloys must be overcome with powerful etchants. The processes which utilize concentrated beam energy or electric discharge cause metal removal by very concentrated melting and vaporization; they are often capable of producing the requisite accuracy, but adverse metal workpiece.

To describe the problems more specifically by example, in making holes by laser or electron beam drilling, a beam is impinged in concentrated form on a cast airfoil workpiece surface until it penetrates through. In the process metal is melted and vaporized by the intense beam energy, creating the hole. The intensity of these processes is such that molten and vaporized metal is expelled from the hole being created, this effect being augmented by the use of a volatilizable backer material at the workpiece exit surface. However, there is usually nonetheless a small quantity of molten metal remaining at points along the periphery or length of the hole. When the beam energy is terminated this molten layer solidifies very rapidly. Thus not only is the metallurgical structure of this "recast" layer different from that of the more controllably cast and slowly cooled airfoil, but the resolidified or recast layer is often characterized by small cracks due to shrinkage. When airfoils with holes having recast layers are used, the imperfect recast layer structure tends to cause premature cracking of the airfoil due to fatigue, compared to the resistance to fatigue which the part would have if the holes lacked the deviant metallurgical structure. Naturally, a great deal of effort has been expended to modify the beam energy drilling processes to eliminate the recast layer, but while it has been minimized it has not been able to be eliminated.

Another example involves the production on a workpiece surface of a pattern of varying depth grooves and depressions. Electric discharge machining is a favored process to produce such surface contours, much as it is favored for three-dimensional die sinking. In electric discharge machining (EDM) a preformed electrode is placed in close proximity to the workpiece and electric spark discharge between the electrode and the workpiece causes vaporization and expulsion of material from the workpiece surface into a surrounding dielectric fluid. When surfaces machined by electric discharge are examined they also are found to have a recast layer comprised of material which was momentarily melted and remains adhered to the surface. Further, EDM surfaces are usually characterized by a certain roughness caused by the erratic nature of the spark discharge and in many instances it is desired to have a smoother surface than is typically producible. Of course, if a general secondary machining operation such as grinding is used to smooth an EDM surface the good accuracy from the EDM process can easily be lost, or costs will be increased.

Thus, it is very much desired to have a process which efficiently removes material but which leaves a surface finish nearly comparable to that of a conventional cast or machined surface.

An object of the invention is to machine a superalloy using a thermal effect process, but without leaving a recast layer or other imperfect surface.

According to the invention the recast layer may be selectively removed using chemical milling and an etchant having the composition by volume percent of

40-60 HNO_3, 5-20 HCl, and 20-55 H_2O, with which is included 0.016-0.025 mole/l $FeCl_3$ and at least 0.008 mole/l $CuSO_4$. Preferably the etchant is 50 HNO_3, 10 HCl and 40 H_2O, with 1.3 g/l $FeCl_3$ and 2.6 g/l $CuSO_4$. The $FeCl_3$ improves removal rate but tends to cause unwanted pitting and intergranular attack. These tendencies are inhibited by the addition of $CuSO_4$; preferably the molar ratio of $CuSO_4$ to $FeCl_3$ is 2:1. The beneficial combination of $FeCl_3$ and $CuSO_4$ is usable in other etchants.

The etchant has a self-limiting feature that is very unique. Only the recast layer is removed and the removal of metal which is not recast is minimal. Gas is evolved during removal (preferably done at 40-80°C) and the cessation of evolution may be used as an indication of the completion of the chemical milling process.

The invention provides a rapid way for removing material from a superalloy since thermal effect processes are exceedingly fast and the chemical milling is very selective and also rapid. Machined superalloy surfaces with surfaces free from adverse metallurgical features are thereby provided.

The foregoing and other objects, features and advantages of the present invention will become more apparent from the following description of preferred embodiments and accompanying drawings.

Figure 1(a) is a planar surface view of the entrance of an oblique laser drilled hole showing a cracked recast layer;

Figure 1(b) shows the hole entrance with the recast layer removed after chemical milling.

Figure 2(a) is a partial longitudinal section through the hole of Figure 1(a) showing the hole wall;

Figure 2(b) shows the hole wall after chemical milling.

Figure 3(a) is a planar surface view of a EDM surface showing the rough recast layer;

Figure 3(b) is the surface after chemical milling.

Figure 4(a) is a cross section through the surface shown in Figure 3(a);

Figure 4(b) is a cross section of the surface in Figure 3(b).

The invention is described hereafter in application to the nickel-base superalloy MAR M-200 + Hf, a nickel-base alloy having the composition by weight percent of 10 Co, 9 Cr, 2 Ti, 5 Al, 12 W, 1 Nb, 2 Hf, 0.15 C, 0.015 B, 0.05 Zr, balance Ni. Limited experiment indicates that the process will be useful for other nickel alloys, especially the superalloys such as IN-100, IN-718 and Astroloy.

In its preferred practice the invention was used to produce both holes of improved quality in airfoil walls, and contoured surfaces on superalloys. The hole drilling will be described first. About 10 holes of 0.7 to 1.3 mm diameter were drilled in the as-cast surface of a hollow airfoil wall workpiece having a thickness of about 2.5 mm; the holes were at different inclinations to the surface and thus ranged in length between 2.5 and 5 mm. A neodymium laser generated pulse radiation at 1.06 micron wavelength was applied to the workpiece entrance surface at an intensity of about 10^7 watts/cm^2, with a pulse duration of about 660 microseconds and rate in the range

0.3 to 1 pulses/second. The exit side of the workpiece had applied thereto a backer of epoxy resin to both absorb energy when the wall is penetrated and prevent damage to other surfaces, and to aid in the expulsion of molted metal from the drilled hole. For the general functions and characteristics of desirable backers for electron beam drilling reference may be made to copending U.S. Patent Application Serial No. 968,594 of Howard et al; the art for laser drilling is analogous. Figure 1(a) is a view of the entrance of the drilled hole on the surface 16 of a workpiece. The beam has impinged on the surface so that the hole slants downward toward the left of the photograph. Around the entrance of the hole can be seen the recast layer 10, containing a prominent crack 12 as well as other cracks. Some other recast layer molten material 14 is on the surface surrounding the hole as well. Figure 2(a) shows a portion of a longitudinal section through the same hole. The specimen has been etched to reveal microstructure and the recast layer 10 which is light colored and featureless compared to the more characteristic cast morphology of the base metal 18 which is more removed from the hole. The recast layer was non-uniform and varied in thickness from about 0.08 to 0.8 mm.

Figures 1(b) and 2(b) are analogous views to Figures 1(a) and 2(a), showing the workpiece after chemical milling which is described in more detail below.

Generally conventional EDM techniques are used to produce a pattern of grooves varying in depth from 2.4 to 2.9 mm and in width from 1.5 to 1.8 mm. But to better illustrate the invention, a rectangular parallel-piped test piece with an entirely EDM surface of about 1.61 sq.cm. on one face was produced. The EDM conditions were nominally: 80 volts DC; 3 amps; a pulse frequency of 3 kilocycles; a capacitance of 1 microfarad; using a carbon electrode with a mineral seal dielectric fluid (Exxon Mentor No. 28, Exxon Corp., Houston, Texas) at 27°C. The foregoing conditions are characteristic of those used for a light roughing mode of operation. To produce a piece with grooves a suitably shaped electrode is prepared, and the EDM parameters adjusted according to the area and other considerations in a manner familiar to those with skill in EDM.

The EDM produced a surface finish (as measured by a surface profilometer) of about 2.0-3.0 root mean square (RMS) mm . Of course better finishes can be obtained in EDM but with undesirably slow rate of material removal. The surface condition of a portion of the EDM surface is shown in planar view in Figure 3(a) and in cross section in Figure 4(a). In the latter figure the lighter recast layer 20 is evident in contrast to the unaffected base metal 22, similarly to the appearance of the laser drilled holes. The recast layer varied in thickness from 0.08 to 0.8 mm.

Removal of material by either laser or EDM are designated herein as "thermal effect processes". By this we mean they are processes in which metal is removed by heating above its melting point and wherein there is a residual recast layer on the workpiece surface. Thus we embrace in the scope of our invention other thermal effect processes including but not limited to those mentioned in the Background.

Both the workpiece with the laser drilled holes and that with the EDM surface were separately immersed in a chemical etchant. The composition of the etchant was as follows:

Conc. HNO_3 (69-71%)	1892 ml	(50 v/o)
Conc. HCl (32.5-38%)	375 ml	(10 v/o)
H_2O	1500 ml	(40 v/o)
$FeCl_3$	1.3 g/l	(0.008 mole/l)
$CuSO_4$	2.6 g/l	(0.017 mole/l)

The workpiece having the laser drilled holes was immersed in the etchant at 77°C; after initially observed gas evolution ceased, the workpiece was removed from the etchant and examined. As shown in Figures 1(b) and 2(b) the recast layer was completely removed from the drilled holes. There was some small degree of general attack on the non-recast areas of the workpiece as evidenced by the Figures and examination showed the 6.55 gm workpiece had lost only about 0.118 gm or 1.8% of its original weight. Thus, the substantial effect of the chemical milling was to only the recast layer, and more uniform, smooth, and crack-free holes were provided.

The workpiece with EDM portions was immersed in the electrolyte at 66°C and heavy gas evolution was evident from the EDM areas. After about 5 minutes the gas evolution substantially ceased and the workpiece was removed. Comparative examination produced the data in Table 1. Basically, only the recast layer was removed and the other parts of the test piece were not affected. The height dimension, defined at one end of the part by the sole EDM surface and at the opposing end by an ordinary machined surface, has a change indicative of the removal of the recast layer and smoothing. The other dimensions, length and width, are indicators of the lack of substantial effect of the process on non-EDM surfaces. Electron micro probe measurement of the surface showed the concentration of W increased and that of Cr decreased slightly (about 20% change for each). This is a superficial effect and regarded as minor in consequence.

Table 1. Comparative Measurements on EDM Workpiece Subjected to Chemical Milling

Feature	Before	After	Change
Surface Finish (RMS mm)	2.0-3.0	1.0-1.5	1.27
Length-mm	11.151	11.138	-0.013
Height (EDM surface)-mm	9.779	9.728	-0.051
Width-mm	5.982	5.982	-0.0000
Surface Chemistry-EDM area	High W	Lower than std. W & Cr	
Surface Chemistry-Base Metal	Std. W & Cr	Same as EDM area	

A very striking aspect of the invention is the self-limiting nature of the chemical milling portion of the process. The evolution of gas (hydrogen) is evidence of substantial metal removal; thus when the gas evolution substantially ceases the quantity of metal being dissolved per unit time is substantially reduced. We have not run sufficient detail experiment, but if the workpiece was maintained in the solution some further gradual and general dissolution probably will take place, given the corrosive nature of the etchant. However, for practical purposes the process is self-limiting and the near-cessation of gas evolution gives a signal that the removal of the undesired recast material is complete. While we made visual observation to sense the diminution of gas evolution, physical or chemical gas sensing devices may be alternately used to signal or automatically effect removal of the workpiece from the etchant, for best efficiency and avoidance of minor attack. Another desirable aspect of the process is that the workpiece is left with an improved surface finish and that the corrosive attack of the workpiece in the areas which are not recast is minimal.

The exact mechanism which provides the chemical milling with its self-limiting feature is not evident. However, it is dependent on the constituents, as there are many seemingly similar electrolytes which do not produce this desired result, including that described in our application Serial No.______, "Chemical Milling of High Tungsten Content Superalloys". (As a matter of note, tungsten segregation in normally cast MAR M-200 base metal, the effects of which the related invention overcomes, does not occur in the rapidly quenched recast layer.) The chemical differences between the recast layer and unaffected workpiece substrate are not very great, although they may contribute. Another speculation is that the rapid cooling rates associated with the thermally effected layers produce a metallurgical structure which is more susceptible to corrosion due to its structure, compared to the more slowly cooled and presumably more equilibrated workpiece structure.

Based on our experiments we believe that the electrolyte constituents may be varied within the following range: by volume percent, 40-60 HNO_3, 5-20 HCl, bal H_2O, in combination with 0.008-0.083 moles/liter $CuSO_4$ and 0.016-0.025 moles/liter $FeCl_3$; where the acids are 69-71% conc. nitric acid and 36.5-38% conc. hydrochloric acid.

In our etchant we include ferric chloride as an additional corrodent to speed the rate of material removal. However, the use of the acids by themselves or in combination with the $FeCl_3$ results in pitting and uneven attack of the material being removed; especially, the grain boundaries are attacked. The addition of $CuSO_4$ above the minimum amount prevents this unwanted attack. As indicated, our solution described only slightly attacks the base metal. However, we have noticed that in the absence of $CuSO_4$, the slight attack of the base metal is accelerated preferentially at the grain boundaries. At least 0.03 moles/liter $CuSO_4$ is added; preferably the molar ratios of $CuSO_4$ and $FeCl_3$ is 2:1. $FeCl_3$ should not be added beyond the indicated range, regardless of the amount of $CuSO_4$, because the inhibiting action of $CuSO_4$ will not be sufficient. On the other hand, the amount of $CuSO_4$ may be increased beyond the indicated range since it is benign. We believe that the combination of $FeCl_3$ and $CuSO_4$ to be novel and significant in chemical removal of superalloys.

The moderately elevated temperature we used is desirable to increase the rate of reaction; apart from our nominal best temperature of 66°C, the process is believed operable between 40-80°C, and we prefer to operate in the range of 60-70°C.

Our invention, as described, combines laser or EDM with uniquely selective chemical milling. Generally, our invention combines a thermal effect process with chemical milling using a specialized etchant. In its best use it provides precision machining and quality of surface condition in nickel alloys, but it will be applicable to other nickel alloy material processing using a thermal effect process where the recast layer is undesirable.

While chemical milling is preferably carried out by immersion as described above, other modes of application may also be utilized. Additionally, wetting agents, thickners and so forth may be included with our etchant, as the user is inclined.

Although this invention has been shown and described with respect to a preferred embodiment, it will be understood by those skilled in the art that various changes in form and detail thereof may be made without departing from the spirit and scope of the claimed invention.

CLAIMS:

1. Process for machining the surface of a nickel-base superalloy workpiece characterizedin in that it comprises:

removing workpiece material using a thermal-effect process which causes melting and vaporization of metal, thereby leaving on the workpiece surface a recast layer, and

contacting the surface from which material is removed with an etchant comprised by volume percent of 40-60 HNO_3, 5-20 HCl, 20-55 H_2O, at least 0.008 moles/liter $CuSO_4$ and 0.016-0.025 moles/liter $FeCl_3$, thereby chemically dissolving the recast layer without substantially removing other workpiece surface material.

2. The process according to claim 1, whereby the thermal-effect process is one utilizing beam energy, such as from a laser or electron beam.

3. The process according to claim 1, characterized in that the thermal-effect process is one utilizing an electric discharge.

4. The process according to claim 2, characterized in that the removal of material produces holes is the workpiece.

5. The process according to claim 1, characterized in that the etchant is maintained at 40-80^{o}C and that it further comprises sensing the completion of removal of the recast layer from a substantial diminution in the evolution of gas at the workpiece.

6. The process according to claim 1, characterized in that the molar ratio of $FeCl_3$ and $CuSO_4$ is maintained at 2:1.

7. The process according to claim 1, characterized in that the etchant consists of about 50 HNO_3, 10 HCl, 40 H_2O, with 1.3 g/l $FeCl_3$ and 2.6 g/l $CuSO_4$.

8. The process according to claims 1 or 7, characterized in that the superalloy is based on MAR M-200.

9. An etchant for carrying out the process according to anyone of the claims 1-8 for chemical milling the recast layer of a nickel-base superalloy characterized

in that it comprises by volume percent of 40-60 HNO_3, 5-20 HCl, 20-55 H_2O, and containing at least 0.008 moles/l $CuSO_4$ and 0.0016 -0.025 moles/l $FeCl_3$.

10. In chemical milling of a superalloy using an aqueous acid solution containing more than 0.0016 moles/liter $FeCl_3$, characterized by the improvement which comprises adding more than 0.008 moles/liter $CuSO_4$, to reduce pitting and intergranular attack of the superalloy.

11. The process according to claim 12, characterized in that the aqueous acid solution contains between 0.016-0.025 moles/liter $FeCl_3$.

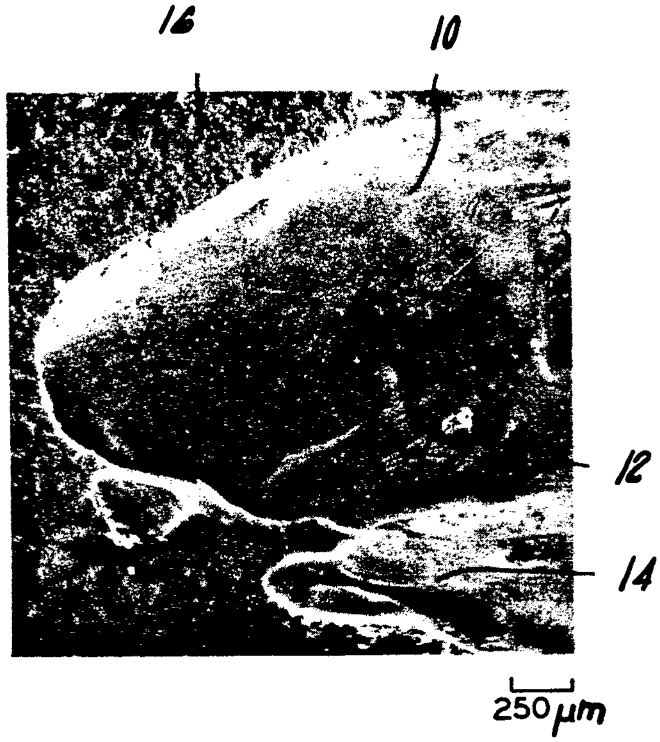


FIG. 1 a DRILLED

FIG. 1b AFTER CHEM-MILL

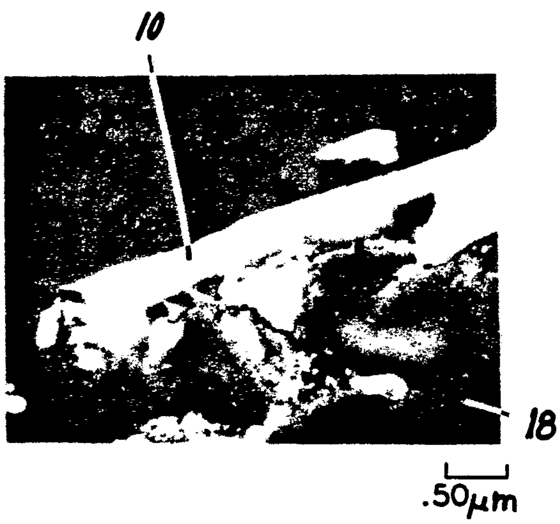
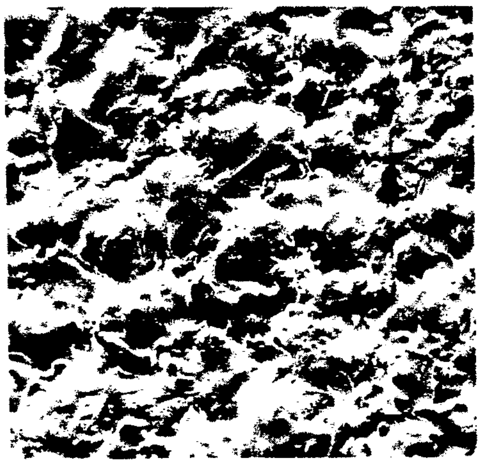


FIG. 2a DRILLED

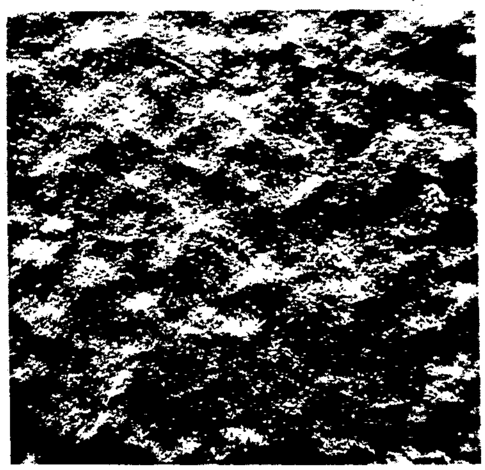
FIG. 2b AFTER CHEM-MILL

FIG. 3a EDM



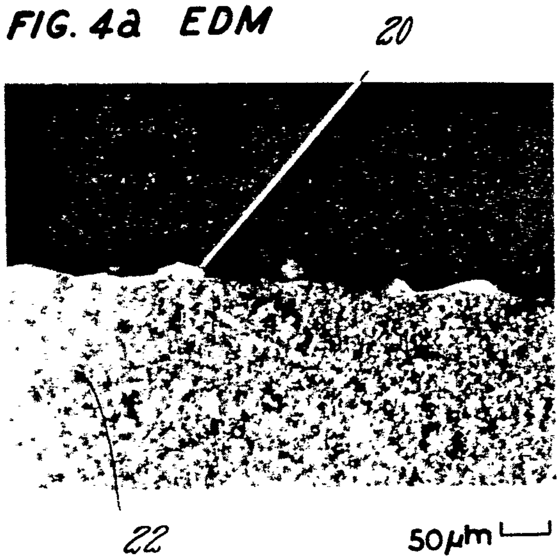
100µm

FIG. 3b AFTER CHEM-MILL



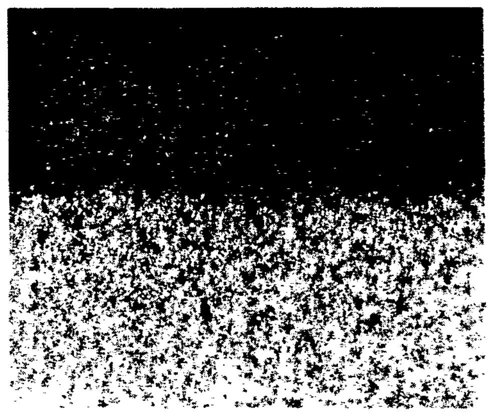
100µm

FIG. 4a EDM



50µm

FIG. 4b AFTER CHEM-MILL



50µm

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European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 81630055.2

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.[3])
	GB - A - 1 353 960 (ROLLS-ROYCE LIMITED) * Page 2; claims * --	1,5	C 23 F 1/00 C 09 K 13/04 C 23 G 1/10
	US - A - 3 467 599 (A.S. PUGLIARISSI) * Abstract; column 3; claims * --	1,5	
	GB - A - 1 475 327 (OXY METAL INDUSTRIES CORPORATION) * Example 2; claims * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.[3])

C 23 F
C 23 G
C 09 K

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	15-12-1981	SLAMA