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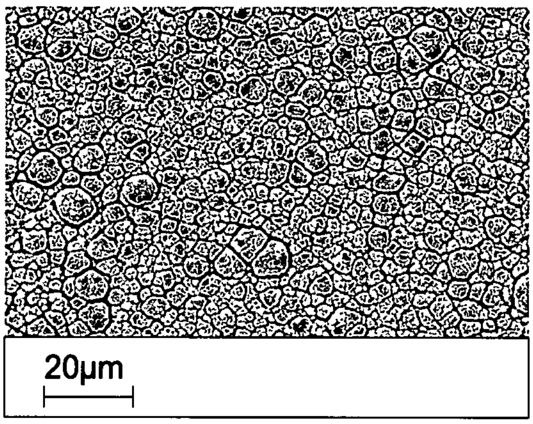


***Fig. 3A***

(57) **Abstract:** Electrochemical etching tailors topography of a nanocrystalline or amorphous metal or alloy, which may be produced by any method including, by electrochemical deposition. Common etching methods can be used. Topography can be controlled by varying parameters that produce the item or the etching parameters or both. The nanocrystalline article has a surface comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others. The active element has a definite spatial distribution in the workpiece, which bears a predecessor spatial relationship to the specified topography. Etching removes a portion of the active element preferentially, to achieve the specified topography. Control is possible regarding: roughness, color, particularly along a spectrum from silver through grey to black, reflectivity and the presence, distribution and number density of pits and channels, as well as their depth, width, size. Processing parameters that have been correlated in the Ni-W system to topography features include, for both the deposition phase and the etching phase of a nanocrystalline surface: duty cycle, current density, deposition duration, plating chemistry, polarity ratio. The relative influence of the processing parameters can be noted and correlated to establish a relationship between values for processing parameters and degree of topography feature. Control can be established over the topography features. Correlation can be made for any such system that exhibits a definite spatial distribution of an active element that bears a predecessor spatial relationship to a desired topography feature.

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# METHODS FOR TAILORING THE SURFACE TOPOGRAPHY OF A NANOCRYSTALLINE OR AMORPHOUS METAL OR ALLOY AND ARTICLES FORMED BY SUCH METHODS

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## RELATED DOCUMENTS

**[0001]** The benefit of U.S. Provisional application No. 60/859,067, filed on November 15, 2006, is hereby claimed, and its entire disclosure is hereby incorporated fully herein, by reference.

## INTRODUCTION

**[0002]** Metals and alloys with nanocrystalline or amorphous structures often exhibit superior physical and/or functional properties, such as high strength, high corrosion-resistance and low coefficient of friction. They may also have desirable magnetic, electronic, optical, or biological properties in specific applications. For these reasons, nanocrystalline or amorphous metals and alloys are gaining wide usage throughout many industries.

**[0003]** Nanocrystalline metal refers to a metallic body in which the number-average size of the crystalline grains is less than one micrometer. The number-average size of the crystalline grains provides equal statistical weight to each grain. The number-average size of the crystalline grains is calculated as the sum of all spherical equivalent grain diameters divided by the total number of grains in a representative volume of the body. Amorphous metal refers to a metallic body without long-range crystalline order, i.e., a metallic body which is solid but not crystalline.

**[0004]** Nanocrystalline or amorphous metals and alloys can be produced by many existing techniques, including severe deformation processing methods, mechanical milling, novel recrystallization or crystallization pathways, vapor phase deposition, and electrochemical deposition (called electrodeposition throughout this disclosure). Electrodeposition is particularly important as a technology for creating nanocrystalline or amorphous metals and alloys, because it can be used to plate out metal on a conductive material of virtually any shape, to yield exceptional surface properties, such as enhanced corrosion and wear resistance and increased yield strength. Such coatings are particularly useful for machine parts, which are subject to high frictional forces, and plastic extrusion molds. At times, within this disclosure and within the claims, the phrase, at most nanocrystalline, is used to mean a metal or alloy having a structure which is either amorphous, or which has the number-average size of any crystalline grains being less than one micrometer or a composite of both.

**[0005]** Nanocrystalline alloys may be constituted, prepared, and deposited according to various methods, such as those described by Detor and Schuh in U.S.S.N. 11/147,146, filed on June 7, 2005, entitled METHOD FOR PRODUCING ALLOY DEPOSITS AND CONTROLLING THE NANOSTRUCTURE THEREOF USING NEGATIVE CURRENT PULSING ELECTRO-DEPOSITION, AND ARTICLES INCORPORATING SUCH DEPOSITS, Attorney Docket No. MIT 11353 US, the full disclosure of which is fully incorporated herein by reference.

**[0006]** In some cases there is a need to tailor the structure or topography of a nanocrystalline or amorphous metal or alloy article surface. For example, a rough surface may be desirable to control the frictional contact with a mating component, (i.e., to improve traction, or reduce contact area, etc.). Alternatively, a controlled surface structure allows a range of optical luster and/or colors. In some cases, the surface topography may require control as part of a micro-manufacturing application, as for example in electroformed stamps or embossing equipment.

[0007] In some cases, surface crevices or pits may be desirable to contain a fluid or particulate medium, as for lubricated surfaces for sliding. The terms pits, pores and voids are all used herein interchangeably to mean a region of a surface that is open, devoid of the substance that makes up the body of the material, and having an opening shape that has a length and width that are of the same order in size. In general, the term pit will be used. An extension on this last concept is for the creation of self-lubricating surfaces, in which surface pits or crevices are filled with a lubricant, and then covered over, as for example by electroplating. Other functional secondary components can be incorporated into a nanocrystalline or amorphous metal in this way. Similar control over surfaces may be useful to improve joining operations such as brazing. In still other cases, increasing the surface area through roughening or through the controlled introduction of surface topography may be desirable for catalytic properties or for increasing the amount of active surface area. In the case of biological implants, porous surfaces are desirable for the in-growth of biological cells and tissues into the implants. Many other possible applications exist or will come to be, in which control over the surface topography of a nanocrystalline or amorphous metal or alloy would be required or desirable.

[0008] A particularly pertinent example of the use for a surface structuring method for nanocrystalline or amorphous metal or alloy is in the area of tribological coatings. In many applications, nanocrystalline or amorphous metal or alloy coatings are being considered for applications where, formerly, chromium coatings were used. For example, as compared to chromium, electrochemically deposited nanocrystalline nickel-tungsten (Ni-W) alloys exhibit many superior properties, such as higher hardness, higher corrosion-resistance and lower coefficient of friction; thus making them better coating materials. Traditionally, chromium would be selected in these applications for its high corrosion resistance and low coefficient of friction. In the area of chromium coatings, a reverse current etch process is commonly employed to create pits that can trap lubricants on the surfaces of chromium coatings, thus further reducing frictional effects in service of the coating. The chromium film is sometimes covered with a perforated insulating sleeve during reverse current etching. The regions of the chromium film that are not covered by the sleeve are etched, leading to the formation of pits on the chromium film. Thus, the size and density of the pits are directly controlled by varying the corresponding parameters of the perforations.

[0009] Another common existing method of imparting a desired surface topography to a component is to apply a texture prior to coating the component with chromium. Thus, techniques like mechanical abrasion, electro-discharge surface texturing, shot peening, sand blasting, etc. are used to create a desirable surface texture or article surface topography. These treatments may (or may not) be followed by the application of a coating which, to at least some extent, replicates the topography of the material beneath, leading to a coated component with a desired surface topography or texture.

[0010] Thus, there are numerous areas where coatings having a specific topography can be useful. And, in particular, it would be desirable to use nanocyrstalline coatings, or deposits in many of these cases, such as nickel-tungsten. In the case where a nanocrystalline or amorphous metal or alloy coating is used in a similar application to a chromium coating made with such a sleeve, there is need for a complementary process to tailor the surface topography. It would be even further desirable if the size, shape, and number density of pits could be controlled in the nanocrystalline or amorphous metal or alloy surface without requiring the use of a perforated sleeve in the etching process. Further, it would be desirable to be able to provide such tailored surfaces with other metal systems, than nickel-tungsten. Further, it is desirable that control over the surface topography be achievable by adjusting more than one stage of a production process, independently. In this manner, it might be possible to achieve the same result in two different manners, which may be useful in situations where one or the other pathway is not available, for unrelated reasons.

## BRIEF DESCRIPTION OF THE FIGURES

**[0011]** These and other objects of inventions defined by the claims attached hereto, and claimed herein, will be more fully understood with reference to the following detailed descriptions, and the Figures of the Drawing, which are:

**[0012]** Fig. 1 is a schematic representation of components of processes to tailor surface morphology of nanocrystalline or amorphous metal or alloy;

**[0013]** Fig. 2A is a digital image of a Scanning Electron Micrograph (SEM) of Ni-W film electrochemically deposited using a 100% duty cycle and with a current density of 0.2 $A/cm^2$;

**[0014]** Fig. 2B is a digital image of an SEM of Ni-W film electrochemically deposited using a 25% duty cycle and with a current density of 0.2 $A/cm^2$;

**[0015]** Fig. 3A is a digital image of an SEM of Ni-W film after reverse current etching, the deposit having been made using a high (100%) deposition phase duty cycle, a current density of 0.2$A/cm^2$, and etching having been done with a 30% duty cycle and with a current density of 0.1 $A/cm^2$;

**[0016]** Fig. 3B is a digital image of an SEM of Ni-W film after reverse current etching, the deposit having been made using a low (25%) deposition phase duty cycle a current density of 0.2A/cm$^2$ and the other parameters the same as was for Fig. 3A;

**[0017]** Fig. 4 is a digital image of an SEM of Ni-W film formed using a 0.2A/cm$^2$ electrochemical deposition current at 12.5% duty cycle for 400 minutes after reverse current etching under the same conditions as for Figs. 3A and 3B;

**[0018]** Fig. 5A is a digital image of an SEM of Ni-W film deposited with a 0.2A/cm$^2$ at 25% duty cycle for 200 minutes after reverse current etching with a 50% etching duty cycle and a current density of O.lA/cm$^2$;

**[0019]** Fig. 5B is a digital image of an SEM of Ni-W film deposited with a current duty of 0.2A/cm$^2$ at 25% duty cycle after reverse current etching with a 30% etching duty cycle and current density of O.lA/cm$^2$ (which is the same as Fig. 3B, shown here for purposes of a different comparison);

**[0020]** Fig. 6A is a digital image of an SEM of Ni-W film deposited at 0.2A/cm$^2$ current density at 100% duty cycle after reverse current etching with a current density of 0.2A/cm$^2$ with a duty cycle of 30%;

**[0021]** Fig. 6B is a digital image of an SEM of Ni-W film after reverse current etching, the deposit having been made using a high (100%) deposition phase duty cycle at 0.2A/cm$^2$, and etching having been done with a 30% duty cycle and with a current density of O.lA/cm$^2$ (which is the same as Fig. 3A, shown here for purposes of a different comparison); and

**[0022]** Fig. 7 is a digital image of an SEM of Ni-W film along a fracture.

# Detailed Description

[0023] Novel technology disclosed here uses etching methods to tailor the surface of a nanocrystalline or amorphous metal or alloy. In a general embodiment of an invention hereof, the nanocrystalline or amorphous metal or alloy may be produced by many existing techniques, including but not limited to severe deformation processing methods, mechanical milling, novel recrystallization or crystallization pathways, vapor phase deposition, and electrodeposition. Common etching methods include but are not limited to dry etching, wet etching, potentiostatic etching, galvanostatic etching and ion beam etching. The surface morphology, or topography, which is used herein synonomously with surface morphology of the nanocrystalline or amorphous metal or alloy, can be controlled by varying the processing parameters or the etching parameters or both. The schematic chart in Fig. 1 summarizes inventions disclosed herein. It illustrates a process of tailoring the surface topography of a nanocrystalline or amorphous metal or alloy article. A more detailed Partial Summary precedes the claims, below.

[0024] Starting from the appropriate precursors (labeled in Fig. 1 as block 'El'), nanocrystalline and amorphous metals or alloys (labeled as blocks 'Ml', 'M2', 'M3'...) can be made via different routes (represented by arrows 'A', 'B', 'C ...). Blocks 'Ml', 'M2' and 'M3' represent nanocrystalline or amorphous metals or alloys of different composition, microstructures and surface morphologies; arrows 'A', 'B' and 'C represent different processing methods and/or parameters. Each nanocrystalline or amorphous metal or alloy, take for example block 'Ml', can in turn be tailored to form nanocrystalline or amorphous metals or alloys of different surface morphologies, as represented in this example by blocks 'Sl', 'S2' and 'S3'. Arrows '1', '2' and '3' represent different etching methods and/or parameters. As represented by arrows '3' and '4', blocks 'Ml' and 'M2', which have different surface morphologies and microstructures, may be tailored to form the same structure 'S3' via different etching processes and/or parameters.

[0025] In general, nanocrystalline or amorphous metals or alloys with different surface morphologies and microstructures may be tailored to form the same end product structure via different etching processes and/or parameters.

[0026] A more specific embodiment of an invention disclosed herein is to couple electrochemical deposition of a nanocrystalline or amorphous structure with electrochemical etching, to introduce a tailored surface. In these embodiments, electrochemical deposition is a particular technique (corresponding to an arrow such as 'A') to form a nanocrystalline or amorphous metal or alloy (corresponding to a block such as 'Ml') from precursor chemicals (corresponding to a block such as 'El'). The process of electrochemical etching (corresponding to an arrow such as '1') is a particular technique to introduce a desirable surface morphology (e.g., 'Sl') into the nanocrystalline or amorphous metal or alloy (e.g., 'Ml').

[0027] Etching is a controlled corrosion process and is a consequence of electrolytic action between surfaces of different potential. (As used herein, electrochemical etching is used to mean galvanostatic etching, potent iometric etching, electro etching and any other electrochemical etching process.) For single-phase nanocrystalline or amorphous metals and alloys, a potential difference exists between grain interiors and grain boundaries, between grains with different orientations, or at concentration gradients in single phase alloys. For alloys, there is generally a potential difference between the elements in the alloy. For multiphase nanocrystalline or amorphous alloys, a potential also exists between the different phases present. In many cases, the more electrochemically positive phase is attacked to a greater extent than the more electrochemically negative phase during etching. Thus, the electrochemically more positive phase is referred to herein as the more electrochemically active phase.

The more electrochemically active phase in many cases is more electrochemically active by virtue of containing a higher proportion of the more electrochemically active element in an alloy. Thus, upon etching the more electrochemically active element is preferentially removed from the surface. It is also helpful to note that the electrochemical activity of the phases or elements depend on the specific chemistry of the medium in which the activities are carried out. Other terms in the art that have also been used to mean the same thing, and are intended to be included within the meaning of electrochemically active phase are electroactive, electropositive, and electromotive. Furthermore, in some alloys, a specific element may be selectively removed during etching in a process called dealloying.

[0028] The extent to which and nature in which a nanocrystalline or amorphous metal or alloy is etched depends on its microstructure (i.e. the arrangement and distribution of the various phases, the orientation of surface areas of different chemical potential, the grain size and shape etc.). Thus, processing parameters of an earlier stage, such as alloy deposition, which affect the microstructure of the nanocrystalline or amorphous metal or alloy, also affect the surface morphology of the subsequently etched nanocrystalline or amorphous metal or alloy. For instance, the surface morphology of a nanocrystalline or amorphous metal or alloy that has high residual stress due to processing is likely to differ appreciably from one that has lower residual stress. Another example is colony formation during electrochemical deposition; by controlling the deposition parameters, surface colony structures of variable sizes and shapes can often be produced in an electrochemical deposit, and upon etching, these preexisting features will influence the final etched surface morphology. (As used herein, electrochemical deposition is used to mean electrodeposit and electrochemical deposition, as those terms are understood in the art.)

[0029] The surface morphology of the etched nanocrystalline or amorphous metal or alloy can also be established by controlling the etching parameters, such as the concentration and type of the etching reagent as in the case of wet or dry etching; the magnitude of the applied potential or current as in the case of potentiostatic or galvanostatic methods, respectively; the temperature and duration of the reaction etc.

[0030] The above paragraphs lay out a basis for some of the inventions disclosed here. The processing parameters affect the microstructure of a nanocrystalline or amorphous metal or alloy, (which in turn influences the extent to which it is etched) . The etching parameters also affect the extent of etching. Thus, the surface morphology of an alloy can be controlled by controlling the deposition and etching parameters, either individually, or both, together. The nanocrystalline or amorphous metal or alloy may be produced by many existing techniques and then etched by a number of different methods; it is by varying the processing and etching parameters that surface morphology may be controlled.

## EXAMPLE

[0031] The use of etching methods to establish the surface morphology of nanocrystalline or amorphous metals or alloys has been reduced to practice for a particular case of a binary alloy of nickel-tungsten. Of the many existing methods that can be used to produce nanocrystalline or amorphous metals or alloys, electrochemical deposition has been used successfully. The electrochemically deposited nanocrystalline nickel-tungsten alloy is etched by a galvanostatic electrochemical etching method.

## ELECTROCHEMICAL DEPOSITION

[0032] The composition of the electrolytic bath, which is maintained at approximately 76°C, is shown in Table 1. The cathode and anode used for electrochemical deposition are a copper substrate and platinum electrode respectively.

| | |
|---|---|
| Nickel sulfate hexahydrate (NiSO4 . 6H2O) | 0.06 M |
| Sodium tungstate hexahydrate (Na2WO4 . 2H2O) | 0.14 M |
| Sodium citrate dihydrate (Na3C6H5O7 . 2H2O) | 0.5 M |
| Ammonium chloride (NH4C1) | 0.5 M |

Table 1: Composition of electrolytic bath

**[0033]** Traditional electrochemical deposition employs a constant steady current between the anode and cathode. With advances in power supply technology, unipolar pulsed current is beginning to take hold in practice. It has been shown that the periodic "off-time" where no current flows benefits the current efficiency, leveling, and stress characteristics of the deposit, thus affecting the surface morphology of the electrochemically deposited film, See generally, Nee, CC, W. Kim, and W. R., *Pulsed Electrodeposition of Ni-Mo Alloys.* Journal of the Electrochemical Society, 1988: p. 1100-1103; Tsai, W.-C, C-C Wan, and Y.-Y. Wang, *Mechanism of copper electrodeposition by pulse current and its relation to current efficiency.* Journal of Applied Electrochemistry, 2002. 32(12): p. 1371-8. The term "duty cycle" describes the fraction of the total time during unipolar pulse plating in which a current flows.

**[0034]** The surface morphology of electrochemically deposited nanocrystalline Ni-W alloys consists of nodular-like structures, which are called colonies. It has been found by the present inventors that the shape of the waveform of the electrochemical deposition current affects the average colony size. (By shape of the waveform, it is meant the shape of a repeating portion of a wave, and also relationships among positive polarity and negative polarity parts of wave forms, the relative duty cycles for each, and the Polarity Ratio, as that term is used in the Detor application, which is fully incorporated by reference herein, above.)

[0035] Figs. 2A and 2B show the surface morphologies of the Ni-W films, which are both electrochemically deposited using an applied current density of 0.2A/cm$^2$. For the film shown in Fig. 2A, the duty cycle of the applied current is 100% and the total duration of the electrochemical deposition process is 30 minutes; for the film shown in Fig. 2B, the duty cycle of the applied current is 25% and the total duration of the electrochemical deposition process is 200 minutes. When viewed optically, the surface of the film in Fig. 2B has a more shiny silver appearance than that in Fig. 2A. For the same amount of effective plating time (duty cycle times total plating time), it can be concluded that the lower the duty cycle, the smaller the size of the nodular colony structure and the smoother and shinier the surface. For the conditions that produced Fig. 2A, the resulting colony structures are on the order of from about 3 μm to 10 μm. For the conditions that produced Fig. 2A, the resulting colony structures are on the order of from about 1 μm and smaller to about 3 μm. Other parameters, such as the current density, polarity ratio, and total duration of the electrochemical deposition process can also influence the surface morphology of the electrochemically deposited nanocrystalline alloy.

[0036] Not only does the shape of the waveform of the current during electrochemical deposition affect the surface morphology of the electrochemically deposited film, but it also affects the surface morphology of the film after it is etched. When the Ni-W films shown in Figs. 2A and 2B are etched under the same conditions using a electrochemical method (as described below), the surface morphologies of the two films differ appreciably. Figs. 3A and B show the etched surface morphology of Ni-W alloy, whose surface morphologies before reverse etching correspond to Figures 2A and 2B respectively. During electrochemical etching, the current density, duty cycle and total duration of the current are O.lA/cm$^2$, 30% and 20 minutes respectively for both films. When viewed optically, it is observed that while the surface of the film in Fig. 3A has a shiny black appearance, the surface of the film shown in Fig. 3B has a shiny silver appearance.

[0037] Experiments are disclosed herein that resulted in surfaces having different colors, primarily black and silver, and intermediates that may be characterized as shades of grey. The surfaces also exhibited reflectivity that have been visually observed and described herein as ranging from dull to shiny. The color and reflectivity of the surfaces can be mere rigorously measured using a standard, such as the CIE L*a*b standard, or any other suitable standard. The numerical measurements of the resulting article surface topography can thus also be correlated to the operating parameters that caused them, deposition and etching duty cycles, deposition and etching current densities, etc., to arrive at a constitutive relationship among the controllable processing parameters and the resultant article surface topographies, so that desired article surface colors and reflectivities can be achieved.

[0038] For films formed using high duty cycles of electrochemical deposition current, the etched surface appears as a network of channels, which surround fully, or partially, nodular structures which are between about 1 μm and 10 μm in width. Each nodular structure is in turn traversed by what appear to be a network of much narrower channels than those which surround the nodular structures at the magnification shown. For films formed using low duty cycles of direct current, generally circular pits appear on the etched surface, having a diameter of about 1 μm to 5 μm, and even larger, where multiple pits have coalesced. Solid ligaments surround and the pits, and run from individual pits to adjacent pits.

[0039] Further reduction of the duty cycle of the electrochemical deposition current decreases both the size and number density of the pits formed during electrochemical etching. Fig. 4 shows the etched surface morphology of a Ni-W film that is formed using a $0.2 A/cm^2$ electrochemical deposition current at 12.5% duty cycle for 400 minutes. The conditions of the electrochemical etching process are the same as the films shown in Figs. 3A and 3B. The surface of the film shown in Fig. 4 has a more shiny silver appearance than that shown in Fig. 3B when viewed optically. Thus, the lower the duty cycle of the electrochemical deposition current, the lower is the density and the smaller is the size of the pits formed after electrochemical etching, and the shinier is the etched surface. The scanning electron micrograph of this specimen (shown in Fig. 4) also reveals clear micro-scale differences in the surface morphology as compared with the samples from Figs. 3A, 3B. In Fig. 4 the surface is characterized by a relatively lower number density of shallow and broad pits; it appears that the width of the pits is between about one and five micrometers, and the spacing between the pits is relatively large, being between one and 20 micrometers. In contrast, In Fig. 3B the spacing between pits is much smaller, being between one and about five micrometers in general.

[0040] In general, the deposition current density may range from about 0.01 A/cm$^2$ to about 1 A/cm$^2$, depending upon the chemistry, temperature, and other conditions used.

[0041] As illustrated with the example of electrochemically deposited nanocrystalline Ni-W alloy, the shape of the waveform of the applied current during electrochemical deposition affects the surface morphology of both the un-etched and etched nanocrystalline alloy. In general, the parameters of the various processing methods that are used to make nanocrystalline or amorphous metals and alloys affect the surface morphology of the etched nanocrystalline or amorphous metal or alloy. All of these tailored surfaces are potentially useful, and these experiments show how the etched surface morphology can be controlled by changing the initial electrochemical deposition process parameters.

ELECTROCHEMICAL ETCHING

[0042] During electrochemical etching, the nanocrystalline or amorphous alloy is an anode of an electrochemical cell.

The applied current flows such that metal atoms in the nanocrystalline or amorphous alloy oxidize into ions and dissolve back into the electrolytic solution. The more reactive metal atoms (i.e. those with higher oxidation potential) will be selectively etched from the nanocrystalline or amorphous alloy. Thus, regions with higher concentrations of the more reactive metal will be etched to a greater extent.

[0043] The electrochemical etching process can be carried out in a different electrolyte from that used for electrochemical deposition. For a Ni-W system, the same electrolytic bath can be used, and a graphite electrode is used as the cathode.

[0044] As in the case of electrochemical deposition, unipolar pulsed current is used during etching in this example. The periodic "off-time," when no current flows, allows the atoms on the nanocrystalline or amorphous alloy surface to diffuse and rearrange. Thus, the duty cycle of the applied current affects the surface morphology of the etched film.

[0045] Figs. 5A and 5B show the effects of the duty cycle of the etching current on nanocrystalline Ni-W electrochemically deposited with a current density of $0.2A/cm^2$ at 25% duty cycle for 200 minutes. (Fig. 5B is the same as Fig. 3B and thus, the conditions of the sample's creation are the same, and is presented here again adjacent Fig. 5A to facilitate comparison.) Whereas the alloy in Fig. 5A is subject to a reverse current with a duty cycle of 50%, that in Fig. 5B is subject to a reverse current with a duty cycle of 30%. The reverse current density in both cases is $O.lA/cm^2$ and the total duration is 20 minutes. It is observed optically that the surface of the film in Fig. 5B has a noticeably more shiny silver appearance than that in Fig. 5A. Thus, other parameters being equal, a higher etching duty cycle in this system results in larger pits, as measured by a representative diameter, and relatively thicker solid regions between pits. The number density of the pits is also relatively lower and the spacing between the pits is generally relatively higher. Conversely, a lower etching duty cycle in this system results in smaller pits, as measured by a representative diameter, and relatively thinner solid regions between pits. The number density of the pits is also relatively higher.

[0046] Other parameters, such as the current density and total duration of the etching process also affect the surface morphology of the etched nanocrystalline alloy. Figs. 6A and 6B show the etched surface morphologies of two Ni-W films that are electrochemically deposited under the same conditions: $0.2A/cm^2$ current at 100% duty cycle for 30 minutes. (Fig. 6B is the same as Fig. 3A and thus, the conditions of the sample's creation are the same, and is presented here again adjacent Fig. 6A to facilitate comparison.) The reverse current density applied with a duty cycle of 30% to the alloy in Fig. 6A is $0.2A/cm^2$ while that applied to the alloy in Fig. 6B is $O.lA/cm^2$. While the surface of the film shown in Fig. 6A has a dull black appearance, the surface of the film shown in Fig. 6B has a shiny black appearance, when viewed optically. Thus, a generally higher etching current density produces a duller, less reflective surface, while a generally lower etching current density produces a shinier, more reflective surface, both of which are black. The reverse current density affects the width of the etched channels and the general pattern of the network formed by the channels on the selectively-etched nanocrystalline alloy. In general, a generally higher etching current density results in wider, more dispersed channels with some relatively large open pits, while a generally lower etching current density produces a relatively finer grain network of relatively narrower width channels, with relatively far fewer pits.

[0047] Based on the above discussion, it is clear that in some particular embodiments of the present invention, not only pits may be formed as part of the surface morphology. The examples shown above reveal conditions under which more complex channel structures may be formed, and these channels may coexist with pits. Channels may be regarded as a specific form of pits with a high degree of spatial correlation (i.e., a row of very closely spaced pits). Therefore, in general, the relations and trends presented in this specification focus on the formation of pits, but can be read more generally to apply to channels, channels in combination with pits, or other surface features. For example, it may in some cases be possible to conduct an etching process composed of two separate sub-processes. In these sub-processes, different etching current densities may be used, or different etching duty cycles, or different etching current waveforms. This could permit the development of multiple different surface topographies or surface features. For example, a combined structure involving both pits and channels might be possible. It is believed that, in general, when elements with different electrochemical activities are spatially distributed, channels form after the etching step. When elements are relatively more uniformly distributed, pits form after the etching step. The number density and shape of these channels or pits will depend on the etching parameters, such as current density and duty cycle.

[0048] As illustrated with the example of electrochemically deposited nanocrystalline Ni-W alloy, the shape of the waveform of the reverse current affects the surface morphology of the etched nanocrystalline alloy. In general, the parameters of the various etching processes, such as wet and dry etching, as well as electrochemical and potentiostatic etching, affect the surface morphology of the etched nanocrystalline or amorphous metal or alloy.

[0049] Depending upon the chemistry, temperature, and other conditions used, the current density employed in electrochemical etching may vary quite broadly, for example over the range 0.001-10 A/cm$^2$. It may also vary as etching continues, as for example if the voltage of the process were regulated rather than the current.

CHEMICAL SEGREGATION TO COLONY BOUNDARIES

**[0050]** Preliminary investigations suggest that the different surface morphologies of the etched electrochemically deposited Ni-W films, as shown in Figs. 3A, 3B and 4, can be attributed to tungsten segregation to the colony boundaries. Prior work by Detor et al. has confirmed W segregation to very small length scales that are characteristic of the grain size (~10nm) See generally, Detor, A. J, and Schuh, C. A., *Solute distribution in nanocrystalline Ni-W alloys examined through atom probe tomography.* Philosophical Magazine, 2006. 86(28): p.4459-75. Since Ni and W have high segregation tendencies, W segregation may also occur to larger length scales that are characteristic of the colony size.

**[0051]** To compare the chemical composition of the colony interior and colony boundary, the as-deposited film, which is electrochemically deposited using a 100% duty cycle forward current is fractured immediately after electrochemical deposition. As shown in Fig. 7, the Ni-W film fractures along the colony boundaries. Energy-dispersive analysis (EDS) and X-ray photoelectron spectroscopy (XPS) analysis are then carried out on the as-deposited surface and the fracture surface. The chemical compositions of these two surfaces correspond to those of the colony interiors and colony boundaries respectively.

**[0052]** The results of the analyses are summarized in Table 2. EDS analysis, which has a depth resolution of -10 microns, shows uniform composition between the as-deposited surface (23.1 at% W) and the fracture surface (23.2 at% W). However, XPS analysis, which has a depth resolution of -IOnm, reveals that the W composition along the fracture surface (31.3 at% W) is significantly higher than that of the as-deposited surface (21.5 at% W). This suggests that W segregates to a high degree along the colony boundary; and that the segregation occurs to a small spatial extent of <10 microns.

| Technique | Depth resolution | Tungsten composition (at%) | |
|---|---|---|---|
| | | As-deposited surface | Fracture surface |
| EDS | ~10 microns | 23.1 | 23.2 |
| XPS | ~10nm | 21.5 | 31.3 |

Table 2: Chemical composition along fracture surface and as-deposited surface of Ni-W electrochemically deposited using 100% duty cycle.

**[0053]** Since W segregates to the colony boundaries and W is electrochemically more reactive than Ni, selective etching of the colony boundaries occurs during reverse-current etching. This results in the surface morphology as shown in Fig. 3A. Because the duty cycle of the applied current during electrochemical deposition affects the size of the colonies (as shown in Figs. 2A and 2B), the duty cycle of the forward current may also affect the degree and spatial extent of W segregation to the colony boundaries. This may, in turn, affect the dealloying behavior of the Ni-W alloys, and thus, result in the different surface morphologies, as shown in Figs. 3A, 3B and 4.

**[0054]** Thus, other matters being equal, in general, segregation trends will arise and this will cause different elements to disperse, with one or another segregating at the grain boundary and colony boundaries. During the etching phase, in general, the electrochemically more active element will depart from the deposit more than will the other elements. Thus, if the more reactive element is preferentially situated at grain boundaries or colony boundaries, then the grain or colony boundaries, as the case may be, will be relatively more etched away than the interiors. If the more active element is away from grain or colony boundaries, more prevalent in the interiors, then the grain or colony interiors will be relatively more etched away than the boundaries. It is believed that the former condition will appear as relatively wider channels throughout the product, while the latter will appear as relatively larger pits, other things being equal.

In the case where segregation occurs to colony boundaries, there are 'triple points' and 'multiple points', where three or more colony boundaries meet on the surface. These points may be preferential etching sites even in comparison to the colony boundaries themselves, leading to the local formation of pits. Thus, controlling the colony size and shape is of interest as it may directly impact the size, spacing, and number density of etch pits.

[0055] Therefore, it is beneficial to control the spatial distribution of the more, or the less electrochemically active element, or, in the case of more complicated systems, the more electrochemically active phase, such as described above by selecting parameters such that the electrochemically active phase segregates preferentially to the grain boundaries. Then it is possible to control the spatial distribution from which material will be removed, because the electrochemically more active phase will be preferentially removed, as compared to less active phases.

[0056] In general, the designer has an engineering purpose to achieve, such as a desired friction condition, or reflectivity condition, or surface area requirement. He identifies a topography, such as a distribution of pits of a given size range, depth range and number density per unit area, to achieve the engineering purpose. The designer then determines a spatial distribution for the most electrochemically active phase, or perhaps phases, prior to etching, which bears a definite, known spatial and predecessor relationship to the specified topography, such that, from experience and considerations such as are disclosed herein, the designer understands that the spatial distribution of the most electrochemically active element, in combination with properly chosen etching processing steps and parameters, would cause or enable the desired topography to arise, either directly or indirectly. Then, the designer chooses parameters for the processing stage of providing an at most nanocrystalline surface, either by: electrochemically depositing, or another suitable method, that will cause the desired spatial distribution to arise before etching. Besides electrochemical deposition, the engineer might also apply thermal treatments or other surface treatments to change the distribution of electrochemically active elements and/or phases. As a result of such choices, the designer now has a set of parameters for providing an at most nanocrystalline surface, which, upon etching, using proper parameters, will cause a topography that will have features that will achieve the engineering purpose. The designer also has in mind parameters for either an electrochemical deposition step, or another processing step, that will provide the at most nanocrystalline surface to use for the etching step.

## ADVANTAGES AND COMMERCIAL APPLICATIONS

[0057] There are many potential applications of etched nanocrystalline or amorphous metal or alloy surfaces. By tailoring the surface morphology of the etched nanocrystalline or amorphous metal or alloy, its roughness can be controlled. Thus, a desired amount of frictional contact between the nanocrystalline or amorphous metal or alloy and a mating component can be achieved. Etched nanocrystalline or amorphous metal or alloy can be used to coat industrial equipment and landing gears of aircraft, where frictional forces between moving parts are of concern. Etched nanocrystalline or amorphous metal or alloy are also ideal for coating dies that are used for plastic extrusion molding. The microscopic surface roughness of the etched film helps to release hot plastic material from a die.

[0058] The roughness of the surface could be measured and quantified using, for example, a profilometer or other roughness measurement system. The roughness could be quantified using the standard $R_a$ measurement, or the root-mean-square or RMS roughness, the density of peaks in the topography, their average height, etc. This roughness could then be correlated to processing parameters, both for a provided workpiece, deposition parameters and etching parameters, to establish a relationship between these properties and finished article roughness.

[0059] The etched surface of the nanocrystalline or amorphous metal or alloy contains surface crevices or pits that can be used to trap a lubricant fluid, such as oil, or particulate medium, such as molybdenum disulphide or carbon. Such lubricated surfaces are ideal for applications where there is a need to reduce friction.

[0060] An extension of this concept is for the creation of self-lubricating surfaces, in which surface pits or crevices are filled with a lubricant, and then covered over, as for example by electroplating. Other functional secondary components can be incorporated into a nanocrystalline or amorphous metal or alloy in this way.

[0061] Traditional metal or alloy coatings are intentionally cracked to trap lubricating substances. In such a case, there is little or no control over the depth of the cracks. Often, the crack propagates through the thickness of the coating film. Corrosion failure occurs when the lubricating fluids trapped in the cracked film are depleted and the underlying substrates exposed to the environment.

[0062] In contrast to traditional coatings, the depth of the crevices or pits of the etched nanocrystalline or amorphous metal or alloy can be controlled by controlling the etching parameters. Thus, corrosion failure can be avoided by making sure that the depth of the pits or crevices is less than the thickness of the nanocrystalline or amorphous metal or alloy

[0063] The size and density of pits on traditional chromium films are controlled primarily, if not exclusively, by controlling the corresponding parameters of the perforations on the insulating sleeve during reverse current etching. This is rather cumbersome and limited in flexibility.

[0064] In contrast, the size, shape, and number density of pits can be controlled according to inventions disclosed herein in the nanocrystalline or amorphous metal or alloy surface without requiring the use of a perforated sleeve in the etching process. For instance, above, examples are related where the size of pits, characterized primarily in the discussion by a width, or diameter, for roughly circular pits, is controlled by changing a parameter, for instance the duty cycle used in the deposition step. As shown with reference to Figs. 3B and 4, the lower the duty cycle of the deposition current, the smaller is the size of the pits formed after etching. Similarly, a higher etching duty cycle results in larger size pits (and thus, conversely, a smaller etching duty cycle results in smaller pits). Although the present work has not quantified a relationship between pit size, as characterized by diameter, and as characterized by depth, qualitative observations are that they are commensurate, at least regarding trends. Thus, a smaller duty cycle for both the depositing and etching steps leads to shallower pits, as well as smaller diameter pits, in general, as discussed.

[0065] A similar situation exists regarding channels, and their widths and depths. As discussed above, in connection with Fig. 6A and 6B, In general, a generally higher etching current density results in wider, more dispersed channels, while a generally lower etching current density produces a relatively finer grain network of relatively narrower width channels. The observed trends are also that the wider channels are also relatively deeper, than the narrower channels, which are relatively shallower. Thus, it can be concluded that a relatively higher etching current density leads to relatively deeper channels.

[0066] Depending on the size and density of the pits or crevices, which can be precisely controlled, the surfaces of the etched nanocrystalline or amorphous metal or alloy can range in appearance from a shiny silver to a uniformly black appearance in the embodiments described above. Additional colors and lusters can also be achievable through variations upon this invention. Thus, a controlled surface structure of the nanocrystalline or amorphous metal or alloy allows a range of optical luster and/or colors.

[0067] Surface-tailored nanocrystalline or amorphous metals or alloys also have applications in micro-manufacturing, as for example in electroformed stamps or embossing equipment.

[0068] Etched nanocrystalline or amorphous metal or alloy may also be useful in joining operations such as brazing.

[0069] In some other cases, etched nanocrystalline or amorphous metal or alloy may have desirable catalytic properties because of their high surface area per volume.

[0070] In the case of biological implants, porous surfaces are desirable for the in-growth of biological cells and tissues into the implants.

[0071] Many other possible applications exist and will arise, in which control over the surface topography of a nanocrystalline or amorphous metals or alloys is required or desirable.

[0072] In some applications, the control of surface roughness and texture is important. Specific root-mean-square roughness values may be desired, a specific density of peaks in the surface topography, controlled numerical roughness parameters, like $R_a$, etc., may all be desired. For example, these parameters might be relevant to tribological performance, or may be important in impressing a desired texture or surface pattern into another material that comes in contact with the nanocrystalline material. For example, polymer sheets, metal sheets, etc., may be printed with surface textures through a contact with a properly structured nanocrystalline or amorphous alloy. The present invention, by allowing the surface texture of amorphous or nanocrystalline alloys to be tuned, in turn allows different impressions on other products.

[0073] Thus, it has been determined that for any given at most nanocrystalline system, the surface topography will depend on parameters during the initial surface creation, for instance by deposition, but also by other means, and also parameters of the etching process. It has been shown, herein, how the values for parameters in electrochemical deposition and electrochemical etching in a Ni-W system, affect end properties. This disclosure has discussed the effects of varying at least the following parameters: deposition duty cycle; deposition current density; relative electrochemical activity of the elements, or higher complexity phases of the deposited surface; etching duty cycle; etching current density; deposition environment (fluid); etching environment (fluid); colony formation properties; affect the surface topography and properties of the etched product, including: roughness; pit size (diameter), pit number density, pit depth, intervening solid network element width; shininess, dullness, blackness, silveryness, reflectivity channel network density (for example, expressed as a linear density of channel length, i.e., length of channel per unit area, or perhaps as an area density, i.e., projected area density of channels per unit area of surface.); channel width; channel depths; and size of solid ligaments between channels.

[0074] The Detor application discusses the effects that varying polarity ratio has on some surface properties, such as nanocrystalline grain size and composition. Thus, varying polarity ratio during an electrochemical depositions phase will also affect the intermediate, un-etched workpiece, and thus, the final article surface topography. Etching can also be done with a non—zero polarity ratio, and it is expected that variations of etching polarity ratio will affect the article surface topography. Thus, both deposition and etching can be conducted using a polarity ratio of between 0 and 1, or could be conducted using D.C. (direct current) or with an on-time and off-time duty cycle, and the on times can be D.C. or can exhibit a variation, which variation can include both positive and negative polarity current, further characterized by a polarity ratio.

[0075] The relationships between each of the parameters' value, and one or more pertinent resultant properties, can be noted and recorded and collated, as has been done with the Ni-W system herein. The collated relationships among the parameters' values, the resultant topographies, and the physical properties that the topographies enable (such as roughness or blackness, just to name two) together establish a constitutive relationship among all of these factors. Then, in designing, and also running a process of producing a product, the relation between the parameters for both the stages of providing, (which may be by electrochemical depositing) an initial at most nanocrystalline surface, and then etching away portions of the surface to achieve a desired end product surface topography, can be exploited, based on the noted and collated trends, or relationships. Thus, for instance, larger pits may be achieved by adjusting one or more of two or more different parameters. These relationships between processing parameters and end results can be determined for any system, and then the values of the parameters can be adjusted to achieve the desired topography.

[0076] Other systems will behave similarly to the Ni-W system, set forth in examples above. Such other systems include: Co-W, Ni-Mo, Co-Mo, Ni-P and Co-P, all substantially binary systems, with the latter mentioned element being more electrochemically active in common electrochemical deposition chemistries. Thus, one might expect that in both the electrochemical deposition and electrochemical etching stages of the processes disclosed herein, similar phenomena will arise from similar trends in parameters, such as duty cycles, current density, polarity ratios, etc.

[0077] Many techniques and aspects of the inventions have been described herein. The person skilled in the art will understand that many of these techniques can be used with other disclosed techniques, even if they have not been specifically described in use together. For instance, the workpiece can be provided either by electrochemical deposition, or some other way, such as by severe mechanical deformation. Once provided, it can be etched. Target article topography properties can be achieved primarily by altering deposition parameters, or, if possible, etching parameters, or both. For instance, shininess is affected by both the deposition duty cycle and the etching duty cycle. A desired degree of shine can be established by adjusting either, or both. Similarly, the size of pits is affected by deposition duty cycle (lower tends to result in smaller pits), as well as etching current density, (again, lower tends to result in smaller pits). Any possible combination of features that are governed by the parameters discussed can be attempted and achieved, such as a shiny black surface exhibiting primarily narrow channels, if the proper combination of parameters can be made without otherwise compromising the requirements of the project under way. The deposition current may be pulsed, steady state, and pulsed with a reversing current that gives rise to a non-zero polarity ratio that is less than one. The etching current may also be pulsed, steady state, or reversing with a polarity ratio. The duty cycles of deposition and etching may be as low as 10%, or as high as 100%.

[0078] The properties mentioned above have been observed in the nickel and tungsten system. Similar properties are expected within the systems mentioned above as having commonality with Ni-W. Other systems may exhibit different properties, or the properties may have other relationships with the processing parameters. However, relationships do and will exist, and they can be determined by methodical observation, which can be collated, categorized, and also put into a relationship between the processing parameters and the topography properties, so that a designer can design a processing system to achieve the desired topography properties.

## PARTIAL SUMMARY OF INVENTIONS

[0079] One invention disclosed herein is a method of making an article having an at most nanocrystalline surface with a specified topography. The method comprises the steps of: providing a workpiece having a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, and which more electrochemically active element has a definite spatial distribution in the workpiece, which definite distribution bears a predecessor spatial relationship to the specified topography. The method includes etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, to achieve the specified topography

[0080] The step of providing a workpiece may comprise electrochemically depositing the at most nanocrystalline material on a substrate to achieve the definite spatial distribution of the more electrochemically active element. If so, the step of electrochemically depositing may comprise electrochemically depositing by using pulsed current, and that may comprise using pulsed current, having a polarity ratio, or, alternatively, direct current, or pulsed current of the same polarity. In such a case, the step of etching may comprise electrochemically etching the surface.

[0081] According to an important embodiment, whether or not the providing step is by electrochemical deposition, the step of etching may comprise electrochemically etching the surface.

[0082] Any etching step may be accomplished using pulsed current, with or without a Polarity Ratio, or using direct current. Thus, either one, both, or neither the depositing step and the etching step may be defined by a polarity ratio.

[0083] With yet another useful embodiment of a method invention hereof, the steps of electrochemically depositing and electrochemically etching both are conducted in an electrolytic liquid. The liquid may be the same liquid, even either by formula, or the same physical volume of liquid, or the liquids may differ.

[0084] According to yet another useful embodiment of a method hereof, the step of electrochemically depositing may be conducted by choosing deposition parameters that promote segregation of the most electrochemically active element to colony boundaries. For instance, the step of choosing parameters may comprise using a relatively larger deposition duty cycle sufficient to promote segregation of the most electrochemically active element to colony boundaries.

[0085] For any of the embodiments discussed, a useful system is where the two elements comprise nickel (Ni) and tungsten (W).

[0086] A particularly advantageous embodiment comprises electrochemically depositing an at most nanocrystalline Ni-W surface.

[0087] According to a generally useful embodiment the step of providing comprises using a pulse current having a current density of between 0.01 $A/cm^2$ and 1.0 $A/cm^2$.

[0088] According to a related useful embodiment the step of etching comprises using a pulse current having a current density of between 0.001 $A/cm^2$ and 10 $A/cm^2$.

[0089] Still another important embodiment of an invention hereof is a method for making an article having an at most nanocrystalline surface with a specified topography, comprising the steps of: providing a workpiece having a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is a metal, and one of which is more electrochemically active than the others; and etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, to achieve the specified topography. With this embodiment, at least one of the following steps is conducted during the providing and etching a workpiece steps. The step of providing a workpiece may be conducted with a value for a parameter for providing, selected with reference to a constitutive relation that relates the providing parameter to the specified surface topography property. Or, the step of etching may be conducted with a value for a parameter for etching, selected with reference to a constitutive relation that relates the etching parameter to the specified surface topography property.

[0090] Or, of course, both of these steps may be conducted together.

[0091] For a closely related embodiment of this method the step of conducting at least one of the steps of: providing a workpiece with a selected parameter value for providing; and etching with a selected etching parameter value, comprises at least one of the steps selected from the group consisting of the following steps.

[0092] Providing the surface by electrochemical deposition, choosing values for parameters of electrochemical deposition to segregate elements of different electrochemical activity preferentially relative to colony boundaries and interiors.

[0093] Electrochemically depositing the surface using a relatively higher depositing duty cycle to achieve relatively larger colony structures.

[0094] Electrochemically depositing the surface using a relatively higher depositing duty cycle to achieve an article topography exhibiting primarily a network of channels.

[0095] Electrochemically depositing the surface using a relatively lower depositing duty cycle to achieve an article topography exhibiting primarily spaced apart pits.

[0096] Electrochemically depositing the surface by using a relatively lower depositing duty cycle to achieve an article topography exhibiting a relatively lower number density of pits.

[0097] Electrochemically depositing the surface by using a relatively lower depositing duty cycle to achieve an article topography exhibiting relatively smaller diameter pits.

[0098] Electrochemically depositing by using a relatively lower depositing duty cycle to achieve an article topography exhibiting a relatively shinier surface.

[0099] Electrochemically etching using a relatively higher etching duty cycle to achieve an article topography exhibiting primarily relatively larger diameter pits.

[00100] Etching electrochemically using a relatively higher etching duty cycle to achieve an article topography exhibiting primarily a relatively lower number density of pits.

[00101] Electrochemically etching using a relatively higher etching duty cycle to achieve an article topography exhibiting primarily relatively thicker solid ligaments between pits.

[00102] Electrochemically etching using a relatively higher etching duty cycle to achieve an article topography exhibiting primarily a relatively duller, and relatively blacker appearance .

[00103] Electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting a relatively duller appearance.

[00104] Electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily relatively wider channels.

[00105] Electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily relatively larger pits.

[00106] Electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily a relatively larger number density of pits.

[00107] Electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily a relatively blacker surface.

[00108] Electrochemically etching using a relatively higher etching duty cycle to achieve an article topography exhibiting primarily relatively deeper pits.

[00109] Electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily relatively deeper pits.

[00110] Electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily relatively deeper channels.

[00111] Yet another important invention disclosed herein is a method for making an article having an at most nanocrystalline surface with a topography having a plurality of spaced apart pits, comprising the steps of: providing a workpiece having a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is a metal, and one of which is more electrochemically active than the others, the more electrochemically active element having a definite surface spatial distribution that bears a predecessor relationship to a topography having a plurality of spaced apart pits; and sleevelessly electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, exploiting the spatial distribution of the more electrochemically active element to achieve the topography having a plurality of spaced apart pits

[00112] A closely related invention is a method for making an article having an at most nanocrystalline surface with a topography having a network of channels. This related method comprises similar steps with the more electrochemically active element having a definite surface spatial distribution that bears a predecessor relationship to a topography having a network of channels; and sleevelessly electrochemically etching the workpiece exploiting the spatial distribution of the more electrochemically active element to achieve the topography exhibiting a network of channels.

[00113] Another closely related invention hereof is a method for making an article having an at most nanocrystalline surface. It comprises the steps of: providing a workpiece having a surface comprising an at most nanocrystalline material, the material having a thickness, and comprising at least two elements, at least one of which is a metal, and one of which is more electrochemically active than the others. It also comprises sleevelessly, electrochemically, etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the surface, to achieve a surface over which is distributed at least one surface feature of the group consisting of: a network of channels; and a plurality of pits; which surface feature has a depth of less than the thickness of the at most nanocrystalline material. The method also includes the step of providing a lubricating material within the at least one surface feature.

[00114] The workpiece can be etched to achieve a surface over which are distributed pits or channels of controlled size, shape or number density, or all of these. The lubricating material may comprise a fluid or a particulate or both.

[00115] A closely related invention hereof is an article having an at most nanocrystalline surface. The article comprises a body portion and at a surface of the body portion, a surface coating comprising an at most nanocrystalline

material, the material having a thickness, and comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others. Distributed over the surface is at least one surface feature, selected from the group consisting of: a network of channels; and a plurality of pits; which surface feature has a depth of less than the thickness of the at most nanocrystalline material; and within the at least one surface feature, a lubricating material. The surface feature may comprise channels or a plurality of pits, or a combination thereof.

[00116] Also an invention disclosed herein is a method of making an article having an at most nanocrystalline surface with a specified roughness. The method comprising the steps of: providing a workpiece having a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, and which more electrochemically active element has a definite spatial distribution in the workpiece, which distribution bears a predecessor spatial relationship to a topography, which topography functionally establishes the specified roughness. The method also comprises the step of electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, values for parameters of etching having been selected with regard to the predecessor relationship to achieve the topography and thus, the specified roughness.

[00117] An invention closely related to this, has the step of providing a workpiece comprising electrochemically depositing an at most nanocrystalline material using parameters of deposition selected to achieve the definite spatial distribution of the more electrochemically active element.

[00118] A general invention hereof is a method of making an article having an at most nanocrystalline surface with a

topography property selected from the group consisting of: roughness, blackness, shininess, number density of pits, size of pits, size of channels and spatial distribution of channels, the property having a specified degree. The method comprises the steps of: providing a workpiece having a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which comprises metal, and one of which is more electrochemically active than the others, and which more electrochemically active element has a definite spatial distribution in the workpiece, which distribution bears a predecessor spatial relationship to a topography, which topography functionally establishes the specified selected property to the specified degree. The method also includes the step of electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, parameters of etching having been selected with regard to the predecessor relationship to achieve the topography and thus, the specified selected property to the specified degree.

**[00119]** There are a number of inventions disclosed herein with respect to individual article properties.

**[00120]** One is a method of making an article having an at most nanocrystalline surface with a specified degree of blackness within a range from black to silver. The method comprises the steps of: providing a workpiece, and electrochemically depositing on the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, by using current, defined by a deposition duty cycle of between about 12.5% and about 100% and a deposition current density of between about O.OlA/$cm^2$ and about 1.0 A/$cm^2$. A relatively higher deposition duty cycle is used to achieve a relatively blacker surface, a relatively lower deposition duty cycle is used to achieve a relatively more silver surface, and a duty cycle intermediate a high duty cycle and a low duty cycle is used to achieve a surface intermediate of black and silver. The deposition stage is followed by electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, by using pulsed current, defined by an etching duty cycle of between about 30% and about 50% and an etching current density, of between about 0.001A/cm$^2$ and about 10.0A/cm$^2$ to achieve the specified blackness.

**[00121]** A closely related embodiment of an invention hereof, further comprises using a high deposition duty cycle to obtain relatively wider channels. A similar related embodiment of an invention hereof, further comprises using a high deposition duty cycle to obtain relatively deeper channels.

**[00122]** Another closely related embodiment of an invention hereof uses a high deposition current density to achieve similar results as a high deposition duty cycle.

**[00123]** A related embodiment of an invention hereof uses a high deposition duty cycle and a low etching current density to achieve a black surface with relatively narrower and shallower channels. Rather than a low etching current density, a low etching duty cycle has a similar effect of reducing the width or depth of channels.

**[00124]** A very closely related invention is a method of making an article having an at most nanocrystalline surface defined at least in part by at least one of a network of channels and a spatial distribution of pits. The method comprises the steps of: providing a workpiece, and electrochemically depositing on the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, by using current, defined by a deposition duty cycle of between about 12.5% and about 100% and a deposition current density of between about 0.0lA/$cm^2$ and about 1.0 A/$cm^2$. A relatively higher deposition duty cycle is used to achieve a surface exhibiting primarily channels, a relatively lower deposition duty cycle is used to achieve a surface exhibiting primarily a plurality of pits, and a duty cycle intermediate a high duty cycle and a low duty cycle is used to achieve a surface exhibiting both a network of channels and a plurality of pits. The deposition stage is followed by electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, by using pulsed current, defined by an etching duty cycle of between about 30% and about 50% and an etching current density, of between about O.OOlA/$cm^2$ and about 10.0A/$cm^2$ to achieve the specified degree of pits and channels.

[00125] A closely related embodiment of an invention hereof, further comprises using a low deposition duty cycle to obtain a surface exhibiting a plurality of spaced apart pits. Using a low deposition duty cycle with a high etching duty cycle, achieves a plurality of pits that are wide, or deep, or in a lower number density, or any of these three properties in combination. Using a low deposition duty cycle with a high etching current density achieves similar results to that just mentioned with high etching duty cycle. Further, such methods produce thicker ligaments between pits.

[00126] Yet another related invention is a method using a low deposition duty cycle with a low etching duty cycle, which achieves a plurality of pits that are relatively narrower, or shallower, or having a higher number density, or any of these three properties. Rather than using a low etching duty cycle, a low etching current density may be used to similar effect.

[00127] Finally, along this vein, rather than using a low deposition duty cycle, using a low deposition current density provides similar results to using a low deposition current density. Practicing the invention with both parameters at low value further directs the trends discussed.

**[00128]** Yet another related invention finds the step of electrochemically depositing comprising using such pulsed current to deposit a surface comprising nodular colonies, using a relatively higher deposition duty cycle to achieve nodular colonies having relatively smaller average size and relatively lower deposition duty cycle to achieve nodular colonies having relatively larger average size, and a duty cycle intermediate a high duty cycle and a low duty cycle to achieve nodular colonies having an average size between relatively smaller and relatively larger average sizes.

**[00129]** Another invention is a method of making an article having an at most nanocrystalline surface with a specified degree of shininess within a range from shiny to dull. This method comprises the steps of: providing a workpiece and electrochemically depositing at the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the other, by using current, defined by a deposition duty cycle of between about 12.5% and about 100% and a deposition current density, of between about 0.0lA/$cm^2$ and about l.OA/$cm^2$, using a relatively lower deposition duty cycle to achieve a relatively shinier surface, a relatively higher deposition duty cycle to achieve a relatively duller surface, and a duty cycle intermediate a low duty cycle and a high duty cycle to achieve a surface that is intermediate shiny and dull. The method further comprises the step of electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, by using pulsed current, defined by an etching duty cycle of between about 10% and about 90% and an etching current density, of between about O.OOlA/$cm^2$ and about 10.0A/$cm^2$ to achieve a surface having the specified shininess .

**[00130]** Another invention is a method of making an article having an at most nanocrystalline surface with a specified shininess within a range from shiny to dull. The method comprises the steps of: providing a workpiece, and electrochemically depositing at the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, by using current, defined by a deposition duty cycle of between about 10% and about 100% and a deposition current density of between about O.OlA/cm$^2$ and about l.OA/cm$^2$, using a relatively lower deposition current density to achieve a relatively shinier surface, a relatively higher deposition current density to achieve a relatively duller surface, and a deposition current density intermediate a low current density and a high current density to achieve a surface intermediate shiny and dull. The deposition step is followed by electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, by using pulsed reverse current, defined by an etching duty cycle of between about 10% and about 90% and an etching current density of between about O.OOlA/cm$^2$ and about 10.0A/cm$^2$ to achieve the article surface with the specified shininess.

[00131] Even another invention is a method of making an article having an at most nanocrystalline surface with a specified topography ranging from relatively larger pits bounded by relatively thicker solid ligaments to relatively smaller pits bounded by relatively thinner solid ligaments. The method comprises the steps of: providing a workpiece; and electrochemically depositing at the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, by using pulsed current, defined by a deposition duty cycle of between about 12.5% and about 100% and a deposition current density of between about 0.0lA/cm$^2$ and about l.OA/cm$^2$. The deposition step is followed by electrochemically etching the workpiece to remove a portion of the more electrochemically

active element preferentially, as compared to any other components of the workpiece, by using pulsed reverse current, defined by an etching duty cycle of between about 10% and about 90% and an etching current density of between about O.OOlA/$cm^2$ and about 10.0A/$cm^2$ to achieve the specified topography, using a relatively higher etching duty cycle to achieve a topography exhibiting primarily relatively larger pits bounded by relatively thicker solid ligaments and by using relatively lower etching duty cycle to achieve a topography exhibiting primarily relatively smaller pits bounded by relatively thinner solid ligaments.

**[00132]** Last but also important is a method of making an article having an at most nanocrystalline surface with a specified topography ranging from a network of relatively wider, irregular channels connecting pits to a network of relatively narrower channels. The method comprising the steps of: providing a workpiece; and electrochemically depositing at the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, by using current, defined by a deposition duty cycle of between about 12.5% and about 100% and a deposition current density of between about 0.0lA/$cm^2$ and about l.OA/$cm^2$. The deposition step is followed by electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, by using pulsed current, defined by an etching duty cycle of between about 10% and about 90% and an etching current density of between about 0.00lA/$cm^2$ and about 10.0A/$cm^2$ to achieve the specified topography, using a relatively higher etching current density to achieve a topography exhibiting a network of relatively wider, irregular channels connecting pits and a relatively lower etching current density to achieve a network of relatively narrower channels.

[00133] This disclosure describes and discloses more than one invention. The inventions are set forth in the claims of this and related documents, not only as filed, but also as developed during prosecution of any patent application based on this disclosure. The inventors intend to claim all of the various inventions to the limits permitted by the prior art, as it is subsequently determined to be. No feature described herein is essential to each invention disclosed herein. Thus, the inventors intend that no features described herein, but not claimed in any particular claim of any patent based on this disclosure, should be incorporated into any such claim.

[00134] Some assemblies of hardware, or groups of steps, are referred to herein as an invention. However, this is not an admission that any such assemblies or groups are necessarily patentably distinct inventions, particularly as contemplated by laws and regulations regarding the number of inventions that will be examined in one patent application, or unity of invention. It is intended to be a short way of saying an embodiment of an invention.

[00135] An abstract is submitted herewith. It is emphasized that this abstract is being provided to comply with the rule requiring an abstract that will allow examiners and other searchers to quickly ascertain the subject matter of the technical disclosure. It is submitted with the understanding that it will not be used to interpret or limit the scope or meaning of the claims, as promised by the Patent Office's rule.

[00136] The foregoing discussion should be understood as illustrative and should not be considered to be limiting in any sense. While the inventions have been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the inventions as defined by the claims.

[00137] The corresponding structures, materials, acts and equivalents of all means or step plus function elements in the claims below are intended to include any structure, material, or acts for performing the functions in combination with other claimed elements as specifically claimed.

[00138] What is claimed is:

# Claims

1. A method of making an article having an at most nanocrystalline surface with a specified topography, the method comprising the steps of:

a. providing a workpiece having a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, and which more electrochemically active element has a definite spatial distribution in the workpiece, which definite distribution bears a predecessor spatial relationship to the specified topography; and

b. etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, to achieve the specified topography.

2. The method of making an article of claim 1, the step of providing a workpiece comprising electrochemically depositing the at most nanocrystalline material on a substrate to achieve the definite spatial distribution of the more electrochemically active element.

3. The method of making an article of claim 2, the step of electrochemically depositing comprising electrochemically depositing by using pulsed current.

4. The method of claim 3, the step of electrochemically depositing comprising using pulsed current, having a polarity ratio.

5. The method of making an article of claim 1, the step of etching comprising electrochemically etching the surface.

6. The method of making an article of claim 2, the step of etching comprising electrochemically etching the surface.

7. The method of making an article of claim 5, the step of etching comprising electrochemically etching using pulsed current.

8. The method of making an article of claim 7, the step of electrochemically etching comprising using pulsed current, having a polarity ratio.

9. The method of making an article of claim 2, the step of electrochemically depositing comprising electrochemically depositing by using pulsed current, having a depositing Polarity Ratio and the step of etching comprising electrochemically etching using pulsed current, having an etching Polarity Ratio.

10. The method of making an article of claim 6, the steps of electrochemically depositing and electrochemically etching both being conducted in an electrolytic liquid.

11. The method of making an article of claim 10, the steps of electrochemically depositing and electrochemically etching both being conducted in the same electrolytic liquid.

12. The method of making an article of claim 10, the steps of electrochemically depositing and electrochemically etching being conducted in different electrolytic liquids.

13. The method of making an article of claim 2, the step of electrochemically depositing being conducted by choosing deposition parameters that promote segregation of the most electrochemically active element to colony boundaries.

14. The method of making an article of claim 13, the step of choosing parameters comprising using a relatively larger duty cycle sufficient to promote segregation of the most electrochemically active element to colony boundaries.

15. The method of claim 1, the two elements comprising nickel (Ni) and tungsten (W).

16. The method of claim 10, the two elements comprising nickel and tungsten.

17. The method of claim 15, the step of providing comprising electrochemically depositing an at most nanocrystalline Ni-W surface.

18. The method of claim 2, the step of providing comprising using a pulse current having a current density of between 0.01 $A/cm^2$ and 1.0 $A/cm^2$

19. A method for making an article having an at most nanocrystalline surface with a specified topography, comprising the steps of:

a. providing a workpiece having a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others; and

b. etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, to achieve the specified topography;

wherein, at least one of the following steps i and ii is conducted during the providing and etching a workpiece steps:

i. the step of providing a workpiece is conducted with a value for a parameter for providing selected with reference to a constitutive relation that relates the providing parameter to the specified surface topography property; and

ii. the step of etching is conducted with a value for a parameter for etching, selected with reference to a constitutive relation that relates the etching parameter to the specified surface topography property.

20. The method of making an article of claim 19, further, wherein the step of conducting at least one of the steps of providing a workpiece with a selected parameter value for providing; and etching with a selected etching parameter value, comprises at least one of the steps selected from the group consisting of:

i. providing the surface by electrochemical deposition, choosing values for parameters of electrochemical deposition to segregate elements of different electrochemical activity preferentially relative to colony boundaries and interiors;

ii. electrochemically depositing the surface using current, having a relatively higher depositing duty cycle to achieve relatively larger colony structures;

iii. electrochemically depositing the surface using current, having a relatively higher depositing duty cycle to achieve an article topography exhibiting primarily a network of channels;

iv. electrochemically depositing the surface using current, having a relatively lower depositing duty cycle to achieve an article topography exhibiting primarily spaced apart pits;

v. electrochemically depositing the surface by using current, having a relatively lower depositing duty cycle to achieve an article topography exhibiting a relatively lower number density of pits;

vi. electrochemically depositing the surface by using current, having a relatively lower depositing duty cycle to achieve an article topography exhibiting relatively smaller diameter pits;

vii. electrochemically depositing by using current, having a relatively lower depositing duty cycle to achieve an article topography exhibiting a relatively shinier surface;

viii. electrochemically etching using current, having a relatively higher etching duty cycle to achieve an article topography exhibiting primarily relatively larger diameter pits;

ix. etching electrochemically using current, having a relatively higher etching duty cycle to achieve an article topography exhibiting primarily a relatively lower number density of pits;

x . electrochemically etching using current, having a relatively higher etching duty cycle to achieve an article topography exhibiting primarily relatively thicker solid ligaments between pits;

xi.- electrochemically etching using current, having a relatively higher etching duty cycle to achieve an article topography exhibiting primarily a relatively duller, and relatively blacker appearance;

xii. electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting a relatively duller appearance;

xiii. electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily relatively wider channels;

xiv. electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily relatively larger pits;

xv. electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily a relatively larger number density of pits;

xvi. electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily a relatively shinier surface;

xvii. electrochemically etching using a relatively higher etching duty cycle to achieve an article topography exhibiting primarily relatively deeper pits;

xviii. electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily relatively deeper pits; and

xix. electrochemically etching using a relatively higher etching current density to achieve an article topography exhibiting primarily relatively deeper channels .

21. A method for making an article having an at most nanocrystalline surface, comprising the steps of:

a. providing a workpiece having a surface comprising an at most nanocrystalline material, the material having a thickness, and comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others;

b. sleevelessly, electrochemically, etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, to achieve a surface over which is distributed at least one surface feature of the group consisting of:

i. a network of channels; and

ii. a plurality of pits;

which surface feature has a depth of less than the thickness of the at most nanocrystalline material; and

c. providing a lubricating material within the at least one surface feature.

22. The method of claim 21, the step of sleevelessly etching comprising etching the workpiece to achieve a surface over which are distributed pits of controlled size.

23. The method of claim 21, the step of sleevelessly etching comprising etching the workpiece to achieve a surface over which are distributed channels of controlled size.

24. The method of claim 21, the step of sleevelessly etching comprising etching the workpiece to achieve a surface over which are distributed pits of controlled shape.

25. The method of claim 21, the step of sleevelessly etching comprising etching the workpiece to achieve a surface

over which are distributed pits at a controlled number density.

26. The method of claim 21, the lubricating material comprising a fluid.

27. The method of claim 21, the lubricating material comprising a particulate.

28. A method of making an article having an at most nanocrystalline surface with a specified roughness, the method comprising the steps of:

a. providing a workpiece having a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, and which more electrochemically active element has a definite spatial distribution in the workpiece, which distribution bears a predecessor spatial relationship to a topography, which topography functionally establishes the specified roughness; and

b. electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, values for parameters of etching having been selected with regard to the predecessor relationship to achieve the topography and thus, the specified roughness.

29. The method of claim 28, the step of providing a workpiece comprising electrochemically depositing an at most nanocrystalline material using parameters of deposition selected to achieve the definite spatial distribution of the more electrochemically active element.

30. A method of making an article having an at most nanocrystalline surface with a topography property selected from the group consisting of: roughness, blackness, shininess, number density of pits, size of pits, and spatial distribution of channels, said property having a specified degree, the method comprising the steps of:

a. providing a workpiece having a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, and which more electrochemically active element has a definite spatial distribution in the workpiece, which distribution bears a predecessor spatial relationship to a topography, which topography functionally establishes the specified selected property to the specified degree; and

b. electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, parameters of etching having been selected with regard to the predecessor relationship to achieve the topography and thus, the specified selected property to the specified degree.

31. An article having an at most nanocrystalline surface, comprising:

a. a body portion;

b. at a surface of the body portion, a surface coating comprising an at most nanocrystalline material, the material having a thickness, and comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others; and

c. distributed over the surface, at least one surface feature, selected from the group consisting of:

i. a network of channels; and

ii. a plurality of pits;

which surface feature has a depth of less than the thickness of the at most nanocrystalline material; and

d. within the at least one surface feature, a lubricating material.

32. The article of claim 31, the surface feature comprising channels.

33. The article of claim 31, the surface feature comprising a plurality of pits.

34. A method for making an article having an at most nanocrystalline surface with a topography having a plurality of spaced apart pits; comprising the steps of:

a. providing a workpiece having a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, the more electrochemically active element having a definite surface spatial distribution that bears a predecessor relationship to a topography having a plurality of spaced apart pits; and

b. sleevelessly electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, exploiting the spatial distribution of the more electrochemically active element to achieve the topography having a plurality of spaced apart pits.

35. A method for making an article having an at most nanocrystalline surface with a topography having a network of channels; comprising the steps of:

a. providing a workpiece having a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, the more electrochemically active element having a definite surface spatial distribution that bears a predecessor relationship to a topography having a network of channels; and

b. sleevelessly electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, exploiting the spatial distribution of the more electrochemically active element to achieve the topography exhibiting a network of channels.

36. A method of making an article having an at most nanocrystalline surface with a specified degree of blackness within a range from black to silver, the method comprising the steps of:

a. providing a workpiece;

b. electrochemically depositing on the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, by using current, defined by a deposition duty cycle of between about 12.5% and about 100% and a deposition current density of between about O.OlA/$cm^2$ and about 1.0 A/$cm^2$, using a relatively higher duty cycle to achieve a relatively blacker surface, a relatively lower deposition duty cycle to achieve a relatively more silver surface, and a duty cycle intermediate a high duty cycle and a low duty cycle to achieve a surface intermediate of black and silver; and

b. electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, by using pulsed current, defined by an etching duty cycle of between about 30% and about 50% and an etching current density, of between about 0.00lA/$cm^2$ and about 10.0A/$cm^2$ to achieve the specified blackness.

37. The method of making an article of claim 36, the step of electrochemically depositing comprising using such pulsed current to deposit a surface comprising nodular colonies, using a relatively higher deposition duty cycle to achieve nodular colonies having relatively smaller average size and relatively lower deposition duty cycle to achieve nodular colonies having relatively larger average size, and a duty cycle intermediate a high duty cycle and a low duty cycle to achieve nodular colonies having an average size between relatively smaller and relatively larger average sizes.

38. A method of making an article having an at most nanocrystalline surface with a specified degree of shininess within a range from shiny to dull the method comprising the steps of:

a. providing a workpiece;

b. electrochemically depositing at the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, by using current, defined by a deposition duty cycle of between about 12.5% and about 100% and a deposition current density, of between about 0.0lA/cm$^2$ and about l.OA/cm$^2$, using a relatively lower deposition duty cycle to achieve a relatively shinier surface, a relatively higher deposition duty cycle to achieve a relatively duller surface, and a duty cycle intermediate a low duty cycle and a high duty cycle to achieve a surface that is intermediate shiny and dull; and

c. electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, by using pulsed current, defined by an etching duty cycle of between about 10% and about 90% and an etching current density, of between about O.OOlA/cm$^2$ and about 10.0A/cm$^2$ to achieve a surface having the specified shininess.

39. A method of making an article having an at most nanocrystalline surface with a specified topography defined at least in part by at least one of a network of channels and a spatial distribution of pits, the method comprising the steps of:

a. providing a workpiece;

b. electrochemically depositing at the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, by using current, defined by a deposition duty cycle of between about 12.5% and about 100% and a deposition current density, of between about O.OlA/$cm^2$ and about l.OA/$cm^2$, using a relatively higher duty cycle to achieve a topography exhibiting primarily a network of channels, a relatively lower deposition duty cycle to achieve a topography exhibiting primarily a distribution of pits, and a duty cycle intermediate a high duty cycle and a low duty cycle to achieve a topography exhibiting both a network of channels and a distribution of pits; and

c. electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, by using pulsed reverse current, defined by an etching duty cycle of between about 30% and about 50% and an etching current density, of between about 0.001A/$cm^2$ and about 10.0A/$cm^2$ to achieve the specified surface topography.

40. The method of making an article of claim 39, the step of electrochemically depositing comprising using such current to deposit a surface, using a relatively lower deposition duty cycle to achieve a distribution after etching of relatively smaller pits and relatively higher deposition duty cycle to achieve a distribution after etching of relatively larger pits.

41. A method of making an article having an at most nanocrystalline surface with a specified shininess within a range from shiny to dull, the method comprising the steps of:

a. providing a workpiece;

b. electrochemically depositing at the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, by using current, defined by a deposition duty cycle of between about 10% and about 100% and a deposition current density of between about O.OlA/cm$^2$ and about l.OA/cm$^2$, using a relatively lower deposition current density to achieve a relatively shinier surface, a relatively higher deposition current density to achieve a relatively duller surface, and a deposition current density intermediate a low current density and a high current density to achieve a surface intermediate shiny and dull; and

c. electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, by using pulsed reverse current, defined by an etching duty cycle of between about 10% and about 90% and an etching current density of between about O.OOlA/cm$^2$ and about 10.0A/cm$^2$ to achieve the article surface with the specified shininess.

42. A method of making an article having an at most nanocrystalline surface with a specified topography ranging from relatively larger pits bounded by relatively thicker solid ligaments to relatively smaller pits bounded by relatively thinner solid ligaments, the method comprising the steps of:

a. providing a workpiece;

b. electrochemically depositing at the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, by using pulsed current, defined by a deposition duty cycle of between about 12.5% and about 100% and a deposition current density of between about O.OlA/cm$^2$ and about l.OA/cm$^2$; and

c. electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, by using pulsed reverse current, defined by an etching duty cycle of between about 10% and about 90% and an etching current density of between about 0.00lA/cm$^2$ and about 10.0A/cm$^2$ to achieve the specified topography, using a relatively higher etching duty cycle to achieve a topography exhibiting primarily relatively larger pits bounded by relatively thicker solid ligaments and by using relatively lower etching duty cycle to achieve a topography exhibiting primarily relatively smaller pits bounded by relatively thinner solid ligaments.

43. A method of making an article having an at most nanocrystalline surface with a specified topography ranging from a network of relatively wider, irregular channels connecting pits to a network of relatively narrower channels, the method comprising the steps of:

a. providing a workpiece;

b. electrochemically depositing at the workpiece, a surface comprising an at most nanocrystalline material comprising at least two elements, at least one of which is metal, and one of which is more electrochemically active than the others, by using current, defined by a deposition duty cycle of between about 12.5% and 100% and a deposition current density of between about O.OlA/cm$^2$ and about l.OA/cm$^2$; and

c. electrochemically etching the workpiece to remove a portion of the more electrochemically active element preferentially, as compared to any other components of the workpiece, by using pulsed current, defined by an etching duty cycle of between about 10% and about 90% and an etching current density of between about 0.001A/cm$^2$ and about 10.0A/cm$^2$ to achieve the specified topography, using a relatively higher etching current density to achieve a topography exhibiting a network of relatively wider, irregular channels connecting pits and a relatively lower etching current density to achieve a network of relatively narrower channels.

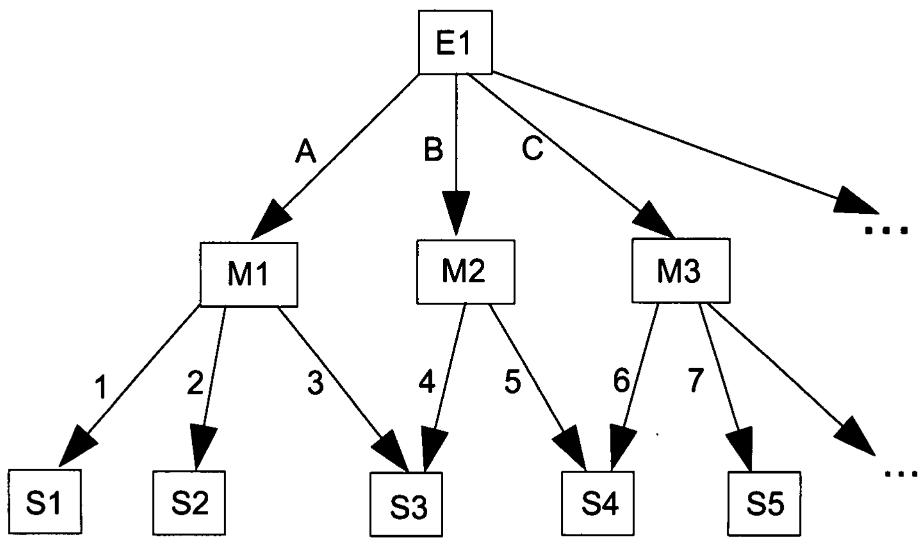


*Fig. 1*

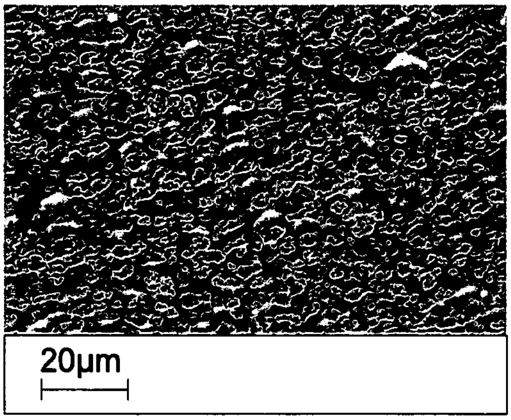


*Fig. 2A*

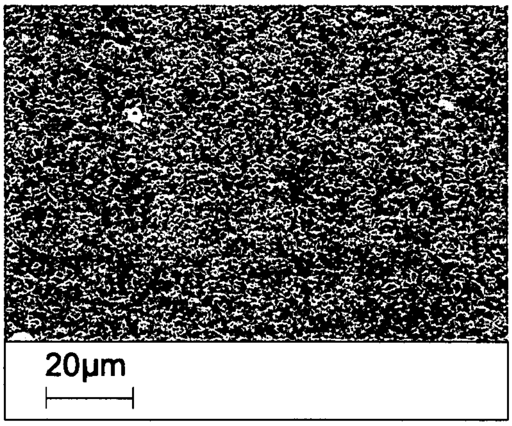


*Fig. 2B*

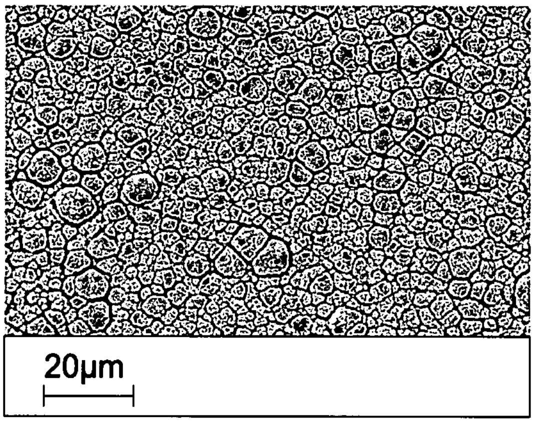


*Fig. 3A*

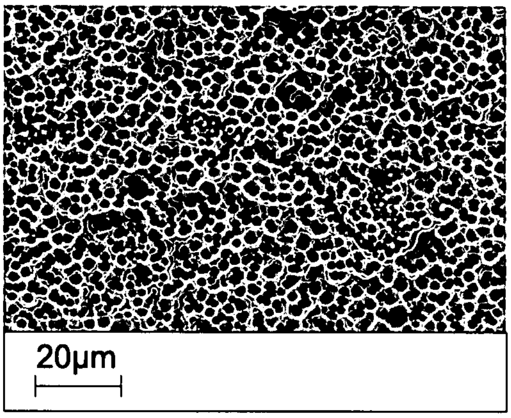


*Fig. 3B*

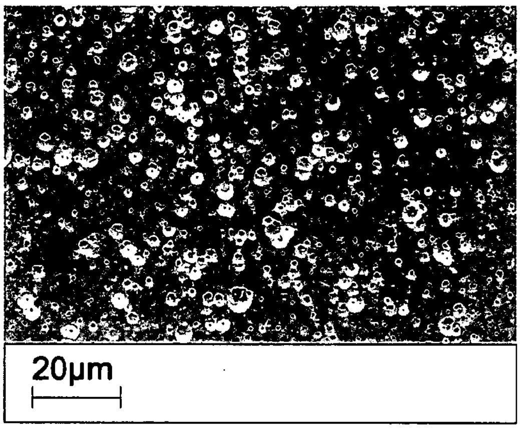


*Fig. 4*

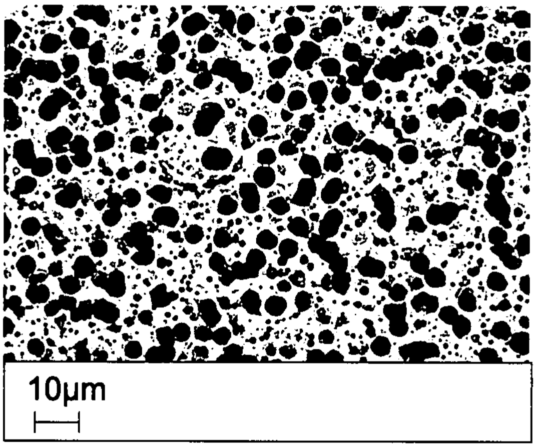


*Fig. 5A*

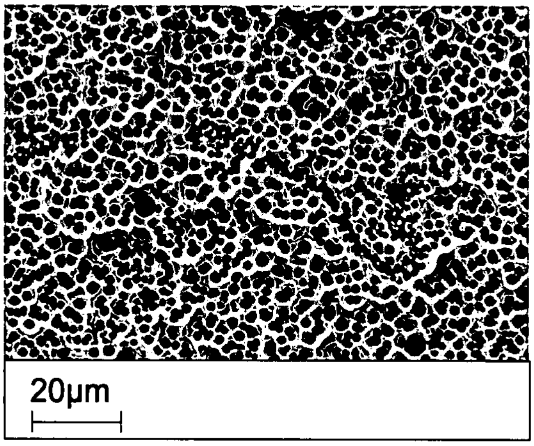


*Fig. 5B*

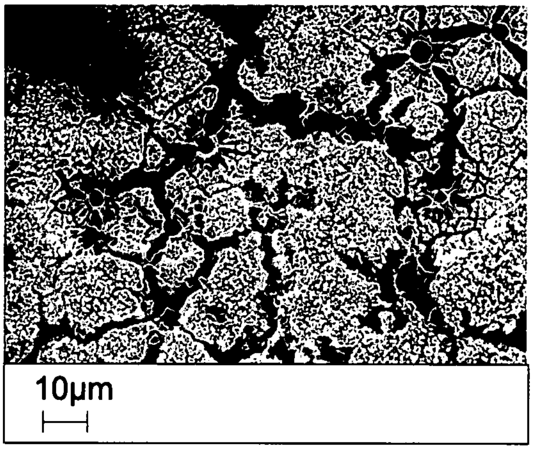


*Fig. 6A*

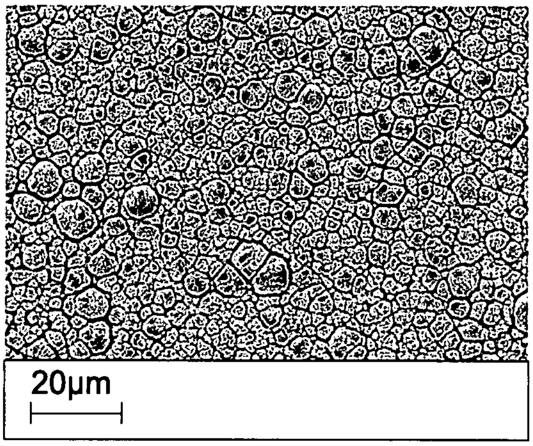


*Fig. 6B*

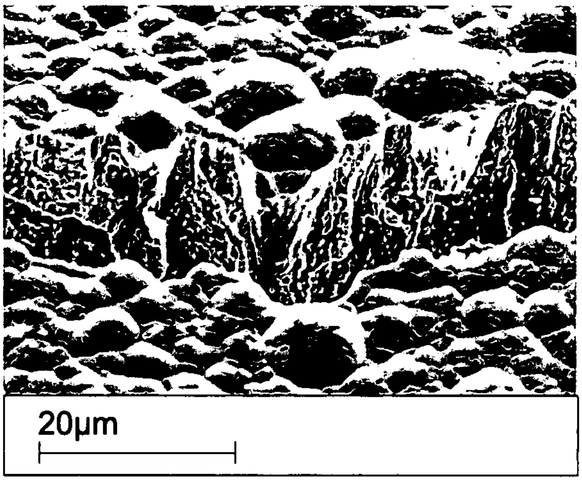


*Fig. 7*

# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/023939

**A. CLASSIFICATION OF SUBJECT MATTER**
INV. C25F3/14 C25F3/08 C25D5/48 C25D5/18

According Io International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
C25D C25F C23F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted dunng the international search (name of data base and, where practical, search terms used)

**EPO-Internal , WPI Data, COMPENDEX**

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category * | Citation of document with indication, where appropriate of the relevant passages | Relevant to claim No |
|---|---|---|
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| Y | claims 1,3,6-11,14,17<br>example 1<br>column 4, line 38 - column 5, last line<br>column 11, lines 31-34<br>----- | 27 |

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[X] Further documents are listed in lhe continuation of Box C

[X] See patent family annex

* Special categories of cited documents

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of trie same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 26 November 2008 | 08/12/2008 |

| Name and mailing address of the ISA/ | Authonzed officer |
|---|---|
| European Patent Office, P B 5818 Patenltean 2<br>NL - 2280 HV HI\|SWI]k<br>Tel (+31-70) 340-2040,<br>Fax (+31-70) 340-3016 | Zech-Agarwal , Nicole |

# INTERNATIONAL SEARCH REPORT

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| X<br><br>Y | WO 2004/111312 A (BOSCH GMBH ROBERT [DE] ; REHBEIN PETER [DE]; HAAS VOLKER [DE]) 23 December 2004 (2004-12-23)<br><br>claims 1,5,8,10<br>page 7, paragraph 2 | 1,2,10, 19, 31-33<br><br>3-9, 12-18, 27, 34-43 |
| Y | DETOR ET AL: "Tailoring and patterning the grain size of nanocrystalline alloys" ACTA MATERIALIA, ELSEVIER, OXFORD, GB, vol. 55, no. 1, 27 October 2006 (2006-10-27), pages 371-379, XP005786826 ISSN: 1359-6454<br>abstract<br>page 372, right-hand column, paragraph 3<br>page 376, left-hand column, paragraph 2 - right-hand column, paragraph 1<br>figures 2,5 | 2-4, 6-18,29, 36-43 |
| Y | US 4 126 934 A (RICHTER GERHARD ET AL) 28 November 1978 (1978-11-28)<br>abstract<br>column 3, lines 58-64<br>column 4, lines 28-42,63-68<br>column 5, lines 7-23,31-54<br>example 2<br>claims 1,3,6,8,11, 13 | 5-12,16, 29, 34-43 |
| X<br><br>Y | EP 0 392 738 A (SIERADZKI KARL [US]; NEWMAN ROGER C [GB]) 17 October 1990 (1990-10-17)<br><br>claims 1,2,6,9,11, 13<br>abstract | 1,5, 19, 20,28, 30,34,35<br>2-4, 6-18,29, 36-43 |
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PCT/US2007/023939

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