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METHOD OF SURFACE-TREATING WORKPIECE

The present invention relates to a method of surface-treating a workpiece by immersing the workpiece in a reactive treating solution of acid, alkali, or the like to cause foreign matter contained in a surface layer of the workpiece to react with and be dissolved in the treating solution so that the foreign matter will be removed from the workpiece.

It is known to surface-treat a workpiece by causing foreign matter on the workpiece, e.g., unwanted materials contained in a surface layer of the workpiece or burrs on the workpiece, to react with and be dissolved in an acid or alkaline aqueous solution so that the foreign matter will be removed from the workpiece.

Carbide tips of an alloy of tungsten and cobalt are manufactured by mixing tungsten and cobalt powders at suitable proportions together with a binder, and thereafter sintering the mixture. The carbide tips thus manufactured tend to retain cobalt and binder particles which are not sintered in interstices. Since the cobalt and binder particles which are left in a surface layer of a carbide tip may prevent the carbide tip from achieving desired properties, it is customary to surface-treat the sintered carbide tip by immersing it



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in a treating solution containing about 1 % of diluted nitric acid for about 10 minutes to cause the cobalt and binder particles to react with and be dissolved in the diluted nitric acid so that they will be removed from the workpiece.

However, if the carbide tip is surface-treated for a long period of time to dissolve the cobalt and binder particles completely, the tungsten-cobalt alloy is liable to be partially eroded by the diluted nitric acid, with the result that the carbide tip may have a reduced mechanical strength where eroded.

There is known an ultrasonic cleaning process for cleaning a workpiece. According to the ultrasonic cleaning process, a workpiece with foreign matter attached to its surface or burrs on its surface is immersed in water in an ultrasonic processing tank, and radiating ultrasonic energy from an ultrasonic vibrator into the water to remove the foreign matter or burrs.

To shorten the time required to ultrasonically clean a workpiece, it has been attempted to supply an acid or alkaline aqueous solution to the ultrasonic processing tank, immersing a workpiece such as a carbide tip in the acid or alkaline aqueous solution, and radiating ultrasonic energy from the ultrasonic vibrator into the aqueous solution to cause foreign matter contained in a surface layer of the workpiece to react with the acid or alkaline aqueous solution so that the foreign matter will be dissolved into the acid or alkaline aqueous solution and removed from the workpiece.



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The radiated ultrasonic energy acts directly on the surface of the workpiece to remove a portion of the foreign matter or burrs therefrom, and the remainder of the foreign matter is removed by reaction with the acid or alkaline aqueous solution. In this manner, the surface treatment of the workpiece is promoted by the radiated ultrasonic energy.

When cavitation bubbles are formed in the acid or alkaline aqueous solution due to different sound pressures upon radiation of the ultrasonic energy into the acid or alkaline aqueous solution, the gas dissolved in the acid or alkaline aqueous solution is vaporized in the cavitation bubbles, resulting in gas bubbles in the acid or alkaline aqueous solution. Since the gas in the gas bubbles resists the surrounding pressure of the aqueous solution, the gas bubbles are less liable to collapse. Therefore, shock waves that are effective to remove the foreign matter or burrs from the workpiece are not generated sufficiently. Even if shock waves are produced, they are dampened by the gas bubbles and prevented from effectively acting to remove the foreign matter or burrs from the workpiece.

It is therefore an object of the present invention to provide a method of surface-treating a workpiece in a reduced period of time to produce a uniform and high-quality workpiece surface by causing foreign matter contained in a surface layer of the workpiece to react with and be dissolved in a reactive treating solution.

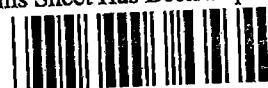


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To achieve the above object, there is provided in accordance with the present invention a method of surface-treating a workpiece, comprising the steps of immersing a workpiece in a reactive treating solution supplied to an ultrasonic processing tank with an ultrasonic vibrator mounted on a bottom thereof, radiating ultrasonic energy from the ultrasonic vibrator into the treating solution to cause foreign matter contained in a surface layer of the workpiece to react with and dissolved in the treating solution, so that the foreign matter will be removed from the workpiece, deaerating the treating solution with a deaerating device by removing a gas dissolved in the treating solution, and supplying the treating solution deaerated by the deaerating device back to the ultrasonic processing tank.

Since the treating solution which reacts with the foreign matter contained in the surface layer of the workpiece is deaerated, the generation of gas bubbles is suppressed when the ultrasonic energy is radiated into the treating solution, allowing a vacuum to be created in cavitation bubbles, which are then easily collapsed under the surrounding pressure thereby to produce intensive shock waves. The shock waves are effective to remove most of the foreign matter contained in the surface layer of the workpiece, and the remainder of the foreign matter reacts with and is dissolved in the treating solution so that it will be removed from the workpiece.

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With the treating solution deaerated, a gas produced when the workpiece reacts with the treating solution is easily dissolved in the treating solution, and does not produce small bubbles which would be attached to the surface of the workpiece. Thus, the reaction between the workpiece and the treating solution is promoted. The radiation of the ultrasonic energy into the treating solution stirs the treating solution for further promotion of the reaction between the workpiece and the treating solution. The time required to treat the surface of the workpiece is therefore greatly reduced.

The treating solution is deaerated by the deaerating device which removes the dissolved gas from the treating solution, and the deaerated treating solution is supplied back to the ultrasonic processing tank. The treating solution supplied to the ultrasonic processing tank remains deaerated at all times.

It is preferable to discharge the treating solution from the ultrasonic processing tank with a discharging device, the deaerating device being positioned downstream of the discharging device, and to supply the treating solution deaerated by the deaerating device back to the ultrasonic processing tank with a supplying device to circulate the treating solution. Use of the treating solution in circulation reduces the amount of reactive treating solution that is discarded, thereby minimizing a harmful effect of the reactive treating solution on the environment.



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The reactive treating solution should preferably be deaerated until the reactive treating solution has a dissolved oxygen content ranging from 0.01 to 5 ppm. If the dissolved oxygen content were in excess of 5 ppm, then it would be impossible to sufficiently suppress the generation of gas bubbles in the treating solution. If the dissolved oxygen content were smaller than 0.01 ppm, then there would be no more advantages than when the dissolved oxygen content ranges from 0.01 to 5 ppm. Specifically, the gas dissolved in the treating solution is air. Since the gases contained in air have substantially constant proportions, the total amount of dissolved gas is represented by the dissolved oxygen content.

It is more preferable to deaerate the reactive treating solution until the reactive treating solution has a dissolved oxygen content ranging from 0.1 to 5 ppm. Inasmuch as the treating solution is reactive and the surface of the workpiece is treated by reaction with the treating solution, the treating solution is not required to be deaerated such a high extent as if the workpiece is ultrasonically cleaned. Thus, the treating solution needs to be deaerated to the above dissolved oxygen content range, and can easily be managed.

The reactive treating solution may comprise an aqueous solution of acid or alkali. The aqueous solution of acid may comprise an aqueous solution of diluted nitric acid. The aqueous solution of alkali may comprise an aqueous solu-



tion of sodium hydroxide. The concentration of the treating solution may be large enough to react with and dissolve the foreign matter contained in the surface layer of the work-piece.

The deaerating device may comprise a gas separating membrane module having a plurality of hollow fibrous gas separating membranes for passing the treating solution therethrough, and an evacuating device for evacuating the gas separating membrane module to develop a pressure difference across the hollow fibrous gas separating membranes. When the hollow fibrous gas separating membranes are evacuated by the evacuating device while the treating solution is flowing through the hollow fibrous gas separating membranes, the pressure outside of the hollow fibrous gas separating membranes becomes lower than the pressure in the hollow fibrous gas separating membranes, discharging the gas dissolved in the treating solution out of the hollow fibrous gas separating membranes. As a consequence, the treating solution is deaerated downstream of the gas separating membrane module, and the deaerated treating solution is supplied back to the ultrasonic processing tank.

The gas separating membrane module is of a simple structure for deaerating the treating solution with high accuracy, and can keep the dissolved oxygen content of the treating solution easily in the above range.

Since the reactive treating solution such as the aqueous solution of acid or alkali is employed in the method



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according to the present invention, the hollow fibrous gas separating membranes tend to be deteriorated during continuous surface treatment. Preferably, the deaerating device should comprise a sealed tank for introducing the treating solution therein, and an evacuating device for evacuating the sealed tank. When the treating solution is introduced into the sealed tank which is evacuated by the evacuating device, the gas dissolved in the treating solution is discharged into the space in the sealed tank, causing the treating solution to be deaerated. Since the deaerating device composed of the sealed tank and the evacuating device has no gas separating membranes, the deaerating device is resistant to acid and alkali, and can deaerate the treating solution sufficiently accurately to the above range.

The above and other objects, features, and advantages of the present invention will become apparent from the following description when taken in conjunction with the accompanying drawings which illustrate a preferred embodiment of the present invention by way of example.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view of an apparatus for carrying out a method of surface-treating a workpiece according to the present invention; and

FIG. 2 is a schematic cross-sectional view of another apparatus for carrying out the method of surface-treating a workpiece according to the present invention.



As shown in FIG. 1, a surface treating apparatus 1 for carrying out a method of surface-treating a workpiece according to the present invention has an ultrasonic processing tank 3 combined with an ultrasonic vibrator 2 mounted on the bottom of the ultrasonic processing tank 3. The ultrasonic processing tank 3 is supplied with an acid or alkaline aqueous solution (treating solution) 4. Workpieces 6 held in a cleaning basket 5 are immersed in the treating solution 4. The ultrasonic vibrator 2 radiates ultrasonic energy into the treating solution 4 to cause foreign matter contained in surface layers of the workpieces 6 to react with and be dissolved in the treating solution 4 so that the foreign matter will be removed from the workpieces 6. To the ultrasonic processing tank 3, there is connected a discharge conduit 7 for discharging the treating solution 4 from the ultrasonic processing tank 3, the discharge conduit 7 being connected to a pump 8 for drawing the treating solution 4 from the ultrasonic processing tank 3. A deaerating device or deaerator 9 is also connected to the discharge conduit 7 downstream of the pump 8 for deaerating the treating solution 4 discharged from the ultrasonic processing tank 3. The treating solution 4 that has been deaerated by the deaerating device 9 is supplied back to the ultrasonic processing tank 3 through a supply conduit 10 that interconnects the deaerating device 9 and the ultrasonic processing tank 3.

The deaerating device 9 comprises a gas separating membrane module 11 having a plurality of hollow fibrous gas



separating membranes for passing the treating solution 4 therethrough, and a vacuum pump 12 for evacuating the gas separating membrane module 11 to develop a pressure difference across the hollow fibrous gas separating membranes.

A surface treating process carried out by the surface treating apparatus 1 shown in FIG. 1 will be described below.

Inventive Example 1

An aqueous solution of 0.1 weight % of diluted nitric acid was supplied as the treating solution 4 to the ultrasonic processing tank 3, and carbide tips of an alloy of tungsten and cobalt were immersed as the workpieces 6 in the treating solution 4 for surface treatment.

Each of the carbide tips 6 was manufactured by sintering tungsten and cobalt powders mixed with a binder, and was of a lozenge shape having a thickness of 3 mm, a width of 15 mm, and a length of 15 mm. The carbide tips 6 carried cobalt and binder particles that have not been sintered and are trapped in interstices of the alloy produced by the sintering process.

The treating solution 4 was supplied through the discharge conduit 7 to the deaerating device 9 by the pump 8 at a rate of 100 liters per hour. The treating solution 4 deaerated by the deaerating device 9 was supplied back to the ultrasonic processing tank 3 through the supply conduit 10. The treating solution 4 in the ultrasonic processing tank 3 contained 2 ppm of dissolved oxygen at all times.



The carbide tips 6 were held by the cleaning basket 5 and immersed in the treating solution 4 thus deaerated. The ultrasonic vibrator 2 radiated ultrasonic energy into the treating solution 4 at a frequency of 28 kHz with an output power of 600 w at a density of 1 w/cm². While the ultrasonic energy was being radiated, the cleaning basket 5 was moved upwardly and downwardly over an interval of 40 mm to allow the ultrasonic energy to act equally on the carbide tips 6. The treating solution 4 was held at 35°C.

After the carbide tips 6 were ultrasonically surface-treated, the cleaning basket 5 was lifted out of the ultrasonic processing tank 3. The carbide tips 6 in the cleaning basket 5 were vertically showered with pure water for 2 minutes, and then dried with hot air at 80°C for 2 minutes.

By being immersed in the treating solution 4 for 1 minute, the surfaces of the carbide tips 6 were uniformly etched by the diluted nitric acid and the cobalt particles were completely removed. It was possible to use the gas separating membrane module 11 in operation continuously for 600 hours.

Comparative Example 1

The same carbide tips 6 as those in *Inventive Example 1* were surface-treated under the same conditions as those in *Inventive Example 1* except that an aqueous solution of 1 weight % of diluted nitric acid was supplied as the treating solution 4 to the ultrasonic processing tank 3, the pump 8 was not operated, and the treating solution 4 was not



deaerated at all by the deaerating device 9. The treating solution 4 in the ultrasonic processing tank 3 contained 6 ppm of dissolved oxygen at all times.

In order to etch the surfaces of the carbide tips 6, the carbide tips 6 had to be immersed in the treating solution 4 for 10 minutes. The surfaces of the carbide tips 6 had deeply pitted regions where the mechanical strength was reduced. The deeply pitted regions appeared to be developed by the etching process that was partly excessively in progress due to the diluted nitric acid.

Comparative Example 2

The same carbide tips 6 as those in *Inventive Example 1* were surface-treated under the same conditions as those in *Inventive Example 1* except that water was supplied as the treating solution 4 to the ultrasonic processing tank 3. As a result, though the carbide tips 6 were immersed in the treating solution 4 for 10 minutes, no etching whatsoever was effected on the carbide tips 6. Only foreign matter attached to the surfaces of the carbide tips 6 was removed by the ultrasonic cleaning. Consequently, almost all cobalt particles in interstices of the alloy of the carbide tips 6 were not removed.

Inventive Example 2

An aqueous solution of 0.1 weight % of sodium hydroxide was supplied as the treating solution 4 to the ultrasonic processing tank 3, and base plates for accommodating hard disk drives (HDD) were immersed as the workpieces 6 in



the treating solution 4 for surface treatment. Each of the base plates 6 was precision die castings of an aluminum alloy, had a box shape having a length of 128 mm, a width of 96 mm, and a depth of 15 mm, and had a wall thickness of 1.2 mm. The base plates 6 had a number of minute burrs on their surfaces.

The base plates 6 were surface-treated under the same conditions as those in *Inventive Example 1* except that the treating solution 4 in the ultrasonic processing tank 3 contained 1.5 ppm of dissolved oxygen and the base plates 6 housed in the cleaning basket 5 were immersed in the deaerated treating solution 4.

As a consequence, the surfaces of the base plates 6 were uniformly etched by the aqueous solution of sodium hydroxide while they were being immersed therein for 1 minute, with the result that all of the minute burrs were dissolved into the aqueous solution and hence removed from the base plates 6. It was possible to use the gas separating membrane module 11 in operation continuously for 1200 hours.

Comparative Example 3

The same base plates 6 as those in *Inventive Example 2* were surface-treated under the same conditions as those in *Inventive Example 1* except that an aqueous solution of 1 weight % of sodium hydroxide was supplied as the treating solution 4 to the ultrasonic processing tank 3, the pump 8 was not operated, and the treating solution 4 was not deaerated at all by the deaerating device 9. The treating



solution 4 in the ultrasonic processing tank 3 contained 6 ppm of dissolved oxygen at all times.

In order to etch the surfaces of the base plates 6, the base plates 6 had to be immersed in the treating solution 4 for 10 minutes. The surfaces of the base plates 6 were partly eroded by the aqueous solution of sodium hydroxide. The erosion appeared to be developed by the etching process that was partly excessively in progress due to the aqueous solution of sodium hydroxide.

Comparative Example 4

The same base plates 6 as those in *Inventive Example 2* were surface-treated under the same conditions as those in *Inventive Example 2* except that water was supplied as the treating solution 4 to the ultrasonic processing tank 3. As a result, though the base plates 6 were immersed in the treating solution 4 for 10 minutes, no etching whatsoever was effected on the base plates 6. Only the minute burrs on the surfaces of the base plates 6 were partly removed by the ultrasonic cleaning.

A surface treating apparatus 21 for carrying out the method of surface-treating a workpiece according to the present invention will be described below with reference to FIG. 2.

The surface treating apparatus 21 shown in FIG. 2 has an ultrasonic processing tank 3 combined with an ultrasonic vibrator 2 mounted on the bottom of the ultrasonic processing tank 3. The ultrasonic processing tank 3 is supplied



with an acid or alkaline aqueous solution (treating solution) 4. Workpieces 6 held in a cleaning basket 5 are immersed in the treating solution 4. The ultrasonic vibrator 2 radiates ultrasonic energy into the treating solution 4 to cause foreign matter contained in surface layers of the workpieces 6 to react with and be dissolved in the treating solution 4 so that the foreign matter will be removed from the workpieces 6. To the ultrasonic processing tank 3, there is connected a discharge conduit 7 for discharging the treating solution 4 from the ultrasonic processing tank 3, the discharge conduit 7 being connected to a discharge pump 22 for drawing the treating solution 4 from the ultrasonic processing tank 3. A deaerating device 23 is also connected through a solenoid-operated valve 24 to the discharge conduit 7 downstream of the discharge pump 22 for deaerating the treating solution 4 discharged from the ultrasonic processing tank 3. The treating solution 4 that has been deaerated by the deaerating device 23 is supplied back to the ultrasonic processing tank 3 through a supply conduit 10 that interconnects the deaerating device 23 and the ultrasonic processing tank 3. The supply conduit 10 is connected to a supply pump 25 which is coupled to the deaerating device 23 through a solenoid-operated valve 26.

The deaerating device 23 comprises a sealed tank 27 for introducing the treating solution 4 therein, and a vacuum pump 28 for evacuating the sealed tank 27. The sealed tank 27 is associated with a level sensor 29 for detecting the



level of the treating solution 4 introduced in the sealed tank 27. The level sensor 29 is electrically connected to the solenoid-operated valves 24, 26.

When the level of the treating solution 4 in the sealed tank 27 reaches a lower level as detected by the level sensor 29, the solenoid-operated valve 24 is opened and the solenoid-operated valve 26 is closed to introduce the treating solution 4 into the sealed tank 27 that has been evacuated by the vacuum pump 28. Upon introduction into the evacuated sealed tank 27, the gas dissolved in the treating solution 4 is discharged into the space in the sealed tank 27, so that the treating solution 4 is deaerated. When the level of the treating solution 4 in the sealed tank 27 reaches an upper level as detected by the level sensor 29, the solenoid-operated valve 24 is closed and the solenoid-operated valve 26 is opened to enable the supply pump 25 to discharge the treating solution 4 from the sealed tank 27. The discharged treating solution 4 is supplied through the supply conduit 10 back to the ultrasonic processing tank 3.

A surface treating process carried out by the surface treating apparatus 21 shown in FIG. 2 will be described below.

Inventive Example 3

An aqueous solution of 10 weight % of diluted nitric acid was supplied as the treating solution 4 to the ultrasonic processing tank 3, and the same carbide tips as



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those in Inventive Example 1 were immersed as the workpieces 6 in the treating solution 4 for surface treatment.

The treating solution 4 was intermittently supplied through the discharge conduit 7 to the deaerating device 10 by the discharge pump 22, and the deaerated treating solution 4 was intermittently supplied through the supply conduit 10 to the ultrasonic processing tank 3 by the supply pump 25. As a result, the treating solution 4 in the ultrasonic processing tank 3 contained 2 ppm of dissolved oxygen at all times.

The carbide tips 6 were held by the cleaning basket 5 and immersed in the treating solution 4 thus deaerated. The ultrasonic vibrator 2 radiated ultrasonic energy into the treating solution 4 at a frequency of 28 kHz with an output power of 600 w at a density of 1 w/cm². While the ultrasonic energy was being radiated, the cleaning basket 5 was moved upwardly and downwardly over an interval of 40 mm to allow the ultrasonic energy to act equally on the carbide tips 6. The treating solution 4 was held at 35°C.

After the carbide tips 6 were ultrasonically surface-treated, the cleaning basket 5 was lifted out of the ultrasonic processing tank 3. The carbide tips 6 in the cleaning basket 5 were rinsed with an upward and downward shower of pure water for 2 minutes, and then dried with hot air at 80°C for 2 minutes.

By being immersed in the treating solution 4 for 30 seconds, the surfaces of the carbide tips 6 were uniformly



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etched by the diluted nitric acid and the cobalt particles were completely removed. The above immersion time of 30 seconds was selected to reliably etch the surfaces of the carbide tips 6. Actually, the uniform etching of the surfaces of the carbide tips 6 was completed within a shorter immersion time. The deaerating device 23 was so resistant to the diluted nitric acid that it suffered no trouble after being continuously used in operation for 600 hours.

Inventive Example 4

The same base plates 6 as those in *Inventive Example 2* were surface-treated under the same conditions as those in *Inventive Example 3* except that an aqueous solution of 10 weight % of sodium hydroxide was supplied as the treating solution 4 to the ultrasonic processing tank 3, the treating solution 4 in the ultrasonic processing tank 3 contained 1.5 ppm of dissolved oxygen at all times, and the base plates 6 housed in the cleaning basket 5 were immersed in the deaerated treating solution 4.

As a consequence, the surfaces of the base plates 6 were uniformly etched by the aqueous solution of sodium hydroxide while they were being immersed therein for 30 seconds, with the result that all of the minute burrs were dissolved into the aqueous solution and hence removed from the base plates 6. The above immersion time of 30 seconds was selected to reliably etch the surfaces of the base plates 6. Actually, the uniform etching of the surfaces of the base plates 6 was completed within a shorter immersion time. The



deaerating device 23 was so resistant to the diluted nitric acid that it suffered no trouble after being continuously used in operation for 1200 hours.

The results of the above examples are given in the following table:

Table

	Work- pieces	Treating solution	Dissolved oxygen (ppm)	Treating time (min)	Re- sult	Continuous operation time (hr)
I. E. 1	Carbide tips	0.1wt%- HNO ₃	2	1	AA	600
I. E. 3	Ditto	10wt%- HNO ₃	2	< 0.5	AA	> 600
C. E. 1	Ditto	1wt%- HNO ₃	6	10	BB	---
C. E. 2	Ditto	Water	2	10	CC	---
I. E. 2	Base plates	0.1wt%- NaOH	1.5	1	AA	1200
I. E. 4	Ditto	10wt%- NaOH	1.5	< 0.5	AA	> 1200
C. E. 3	Ditto	1wt%- NaOH	6	10	BB	---
C. E. 4	Ditto	Water	1.5	10	CC	---

I. E.: Inventive Example

C. E.: Comparative Example

AA: Uniformly etched



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BB: Partly excessively etched

CC: Not etched

It can be seen from Table above that the surface treating method according to the present invention is capable of effecting reaction more uniformly between the workpieces and the treating solution in a shorter period of time with a treating solution of a lower concentration than the surface treating processes in which the reactive treating solution is not deaerated. It is also clear that when water was used as the treating solution instead of the reactive solution, even if it was deaerated in the same manner as the reactive solution, the workpieces were only ultrasonically cleaned as no reaction takes place between the workpieces and the treating solution, resulting in insufficient surface treatment of the workpieces.

When the deaerating device composed of the sealed tank and the vacuum pump (*Inventive Examples 3 and 4*) is used, it is possible to use a treating solution of a higher concentration, shorten the treating time, and surface-treat the workpieces continuously for a longer period of time than when the deaerating device composed of the gas separating membrane module and the vacuum pump (*Inventive Examples 1 and 2*) is used.

Although a certain preferred embodiment of the present invention has been shown and described in detail, it should be understood that various changes and modifications



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may be made therein without departing from the scope of the
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Claims

1. A method of surface-treating a workpiece, comprising the steps of:
 - immersing a workpiece in a reactive treating solution supplied to an ultrasonic processing tank with an ultrasonic vibrator mounted on the bottom thereof;
 - radiating ultrasonic energy from the ultrasonic vibrator into said treating solution to cause foreign matter in a surface layer of the workpiece to react with and dissolve in said treating solution so as to remove the foreign matter from the workpiece;
 - deaerating said treating solution with a deaerating device by removing gas dissolved in the treating solution; and
 - supplying the treating solution deaerated by the deaerating device back to said ultrasonic processing tank.
2. A method as claimed in claim 1, comprising:
 - discharging the treating solution from said ultrasonic processing tank with a discharging device, said deaerating device being positioned downstream of said discharging device; and
 - supplying the treating solution deaerated by the deaerating device back to said ultrasonic processing tank with a supplying device to circulate the treating solution.
3. A method as claimed in claim 1 or claim 2, wherein said reactive treating solution is deaerated until it has a dissolved oxygen content of 0.01 to 5 ppm.
4. A method as claimed in any one of the preceding claims wherein said reactive treating solution is deaerated until it has a dissolved oxygen content of 0.1



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to 5 ppm.

5. A method as claimed in any one of the preceding claims, wherein said reactive treating solution is an aqueous acid solution.

6. A method as claimed in any one of the preceding claims, wherein said reactive treating solution is an aqueous solution of nitric acid.

7. A method as claimed in any one of claims 1 to 4, wherein said reactive treating solution is an aqueous alkali solution.

8. A method as claimed in claim 7, wherein said reactive treating solution is an aqueous solution of sodium hydroxide.

9. A method as claimed in any one of the preceding claims, wherein said deaerating device comprises a gas separating membrane module having a plurality of hollow fibrous gas separating membranes for passing said treating solution therethrough, and an evacuating device for evacuating said gas separating membrane module to develop a pressure difference across said hollow fibrous gas separating membranes.

10. A method as claimed in any one of claims 1 to 8, wherein said deaerating device comprises a sealed tank for introducing said treating solution therein and an evacuating device for evacuating said sealed tank.

