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(54) Title: CASE HARDENING OF TITANIUM

(57) Abstract: A titanium workpiece having a hardened case which is at least 5 microns thick and which is substantially free of titanium nitride is made by contacting the workpiece with a nitriding gas containing nitrogen and a small amount of methane at a temperature of about 700 to 850 °C.



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CASE HARDENING OF TITANIUM

Cross-Reference to Related Application

This case is based on Provisional Application SN 60/360,615, filed February 28, 2002, the disclosure of which is incorporated herein by reference and the benefit of which is hereby claimed.

Field of Invention

The present invention relates to case hardening of titanium by nitrogen diffusion and solid solution.

Background

Titanium and its alloys, like stainless steel, form a coherent oxide coating immediately upon exposure to air. See J.R. Birch and T.D. Burleigh, Corrosion, Vol. 56, No. 12, © 2000, NACE International. As further taught in this reference, this oxide coating is passive (i.e. unreactive) at room temperature. However, when heated up to 600° C, some passivity is lost while at 700° C passivity is significantly less. At 800° C, the oxide coating cracks and spalls.

Although titanium and its alloys are strong, light weight and corrosion resistant at room temperature, they are not particularly hard. Accordingly, considerable efforts have been undertaken to enhance the surface hardness of these metals.

For example, U.S. Patent No. 4,768,757 teaches that a hardened titanium nitride surface layer which is golden in color and up to 2.5 microns thick can be produced by contacting the titanium workpiece with nitrogen gas at about 700° C to 880° C. See, also, U.S. Patent No. 3,656,995 and U.S. Patent No. 5,525,165. Some of these disclosures even indicate that hardened surface coatings as much as 20 microns thick can be obtained. See, for example U.S. Patent No. 4,511,411.

However, the hardened titanium nitride surface layers made in this way tend to exhibit poorer corrosion resistance than the base metal from which the workpiece is made, as determined by contact with 0.5% aqueous hydrofluoric acid. In addition, these hardened surface layers are brittle and rough. Moreover, the fatigue strength of workpieces hardened in this way is lowered because of the crack nucleation sites introduced by this surface roughness. See the Background section of U.S. Patent No. 5,326,362 to Shetty et. al. As a result, this technology is not widely used as a practical matter.

To deal with this problem, the above-noted Shetty Patent describes a modified process in which the workpiece is contacted with nitrogen at temperatures below about 704° C for extended periods of time. Under these conditions, formation of titanium nitride is restricted to an extremely thin surface layer no more than 0.2 microns thick. In addition, a hardened case layer

up to several microns thick and free of titanium nitride forms below the titanium nitride surface layer by a solid solution hardening mechanism from diffused nitrogen, oxygen and carbon. According to patentees, the fatigue strength of workpieces hardened in this way show only minimal adverse effect.

Although Shetty's technology shows promise, the hardened case formed is only several microns thick. Moreover, because of the low temperatures involved, reaction times are slow and hence the process is expensive.

Accordingly, it is desirable to provide new technology for hardening titanium metal and its alloys which provides a hardened case layer which is essentially free of titanium nitride and which is substantially thicker than the "several" micron nitride-free coatings produced in the past by the technology of the above-noted Shetty et al. Patent.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been found that a hardened, corrosion resistant case 5 or more microns thick and containing substantially no titanium nitride can be produced in a titanium workpiece by contacting the workpiece with nitrogen and methane at temperatures above about 704° C for a time sufficient for molecular nitrogen to diffuse into the workpiece surfaces and produce a hardened case of a desired thickness by a solution hardening mechanism.

In particular, it has been found that the tendency of titanium to form titanium nitride coatings when contacted with nitrogen at temperatures above the maximum operating temperature of the Shetty Patent, 704° C, can be minimized and even substantially avoided by including a small but suitable amount of methane or analog in the nitriding gas. Thus, it is possible in accordance with the present invention to produce nitride-free hardened case layers like those described in the Shetty Patent but at higher temperatures, and to a much greater depth, than contemplated in that patent.

Thus, the present invention provides a new article of manufacture comprising a titanium or a titanium alloy workpiece having a hardened case essentially free of titanium nitride and having a resistance to corrosion by 0.5% aqueous hydrofluoric acid greater than that of the metal from which the workpiece, the hardened case being at least about 5 microns thick.

In addition, the present invention provides a new process for case hardening a metal workpiece made from titanium or titanium alloy comprising contacting the workpiece with a nitriding gas containing nitrogen and methane or analog at a temperature of about 700 to 850° C for a time sufficient to form a hardened case at least about 5 microns thick, the hardened case being essentially free of titanium nitride.

DETAILED DESCRIPTION

In accordance with the present invention, a titanium workpiece is surface treated to provide both improved hardness and enhanced corrosion resistance by contact with a nitriding gas containing nitrogen and methane or analog at a temperature above about 704° C for a time sufficient to form a hardened case at least about 5 microns thick and being essentially free of titanium nitride.

Titanium and its Alloys

Titanium and its alloys are known to exist in a number of different crystallographic phases. The most common phase, known as the α -phase, is characterized by a hexagonal closely packed structure. As appreciated by metallurgists, metal atoms arranged in this structure define octahedral interstitial sites between atoms. Another phase exhibited by titanium and its alloys is the β -phase. In this phase, the atoms are not hexagonally closely packed. Nor do they define octahedral interstitial sites between atoms. In some alloys, the α - and β -phases exist together. This is known as a duplex phase structure.

The present invention applies to all titanium and titanium alloys exhibiting the α -phase structure at least to some significant degree, typically 30% or more. Thus, the present invention applies to titanium metal (i.e. essentially pure titanium) as well as to titanium alloys composed substantially completely of the α -phase. In addition, the present invention also applies to duplex and other titanium alloys containing somewhat less than 100% α -phase such as 90%, 80%, 70%, 60%, 50%, 40% and even 30% α -phase. Generally, such alloys will contain at least about 90 wt.% titanium, although alloys containing as little as 65 wt.%, 50 wt.% or even 35 wt.% titanium can also be used.

Although not wishing to be bound to any theory, it is believed that surface hardening occurs in accordance with the present invention by diffusion of nitrogen atoms into the octahedral interstitial sites between metal atoms in the titanium metal matrix of α -phase titanium. Therefore, the workpiece to be treated in accordance with the present invention should contain enough metal in this phase to achieve a noticeable improvement in surface hardening as a result of this diffusion effect.

Earlier researchers have also noticed that nitrogen atoms diffuse into the titanium metal matrix during conventional nitriding. However, nitriding in this prior work has been done so as to produce nitride precipitates, i.e. discrete masses of TiN and/or Ti₂N, since it is these precipitated compounds which improve surface hardness. In accordance with the present invention, however, diffused nitrogen atoms by themselves will achieve substantial surface

hardening. Accordingly, the present invention departs from this earlier practice in that nitriding is accomplished to avoid formation of these nitride precipitates to any substantial degree.

In addition to pure titanium metal, titanium alloys containing any other compatible metal can be case hardened in accordance with the present invention. In this context, "compatible metal" means any other metal which will allow the alloy to exist at least partially in the α -phase and which will not otherwise prevent diffusion of nitrogen atoms into the octahedral interstitial sites in these alloys from occurring. Examples of such additional metals are aluminum, vanadium and molybdenum.

Two particular titanium alloys which can be case hardened in accordance with the present invention are Ti-6Al-4V (6 wt.% Al, 4 wt.% V, balance Ti), which is known as "Titanium 64" (also known as "Grade 5 Titanium") and Ti-8Al-1V-1Mo (8 wt.% Al, 1 wt.% V, 1 wt.% Mo, balance Ti), known as "Titanium 811." Titanium 811 exists almost entirely in the α -phase, while Titanium 64 has a duplex phase structure in which the α - and β -phases are present roughly equally. Nonetheless, both alloys show marked enhancements in both surface hardness and corrosion resistance when case hardened by this technology. Any other commercial titanium alloy, whether available today or sometime in the future, is also amenable to processing by the inventive technology, so long as at least some significant amount of the alloy is present in the α -phase, as indicated above.

Nitriding Gas

The nitriding gas used in accordance with the present invention includes at least two components, a nitrogen-containing gas and a carbon-containing gas.

The nitrogen-containing gas supplies nitrogen atoms for producing a hardened case through diffusion of nitrogen atoms into the titanium metal matrix. The preferred nitrogen-containing gas is molecular nitrogen, i.e. N_2 . Commercially-available nitrogen gas, i.e. N_2 , is the cheapest and easiest gas to use for this purpose. Other nitrogen containing gases can also be used provided that, in the amounts and under the conditions used, they do not supply ingredients which would adversely affect the hardened case being formed. Examples of such other gases are ammonia and gaseous HCN, for example.

The second component of the nitriding gas of the present invention is a carbon-containing gas. The carbon-containing gas supplies carbon atoms to the system which, as indicated above, impede the formation of titanium nitride precipitates. As a result, nitriding can be accomplished by the inventive technology much faster than in the Shetty et al. Patent, thereby allowing a much deeper case to be formed than contemplated there. Thus, hardened cases having thicknesses of 40 microns or more can be readily formed by the inventive technology, which is

much thicker than the "several" microns in thickness contemplated by the Shelby Patent. Carbon atoms also diffuse into the titanium metal matrix, at least to some degree, where they appear to act in a manner similar to the diffused nitrogen atoms in the sense of enhancing surface hardness without formation of undesirable precipitates, i.e. titanium carbide precipitates. Typically, the amount of diffused carbon in the case hardened layer produced by the present invention will be less than that of diffused nitrogen.

The preferred carbon-containing gas is methane, i.e. CH_4 . Other carbon-containing gases can also be used provided that, in the amounts and under the conditions used, they do not supply ingredients which would adversely affect the hardened case being formed. Examples of such other carbon-containing gases are ethane, propane and HCN , for example.

Complementary reactant gases, that is gases which may react with the nitrogen-containing gas, carbon-containing gas and/or the workpiece during nitriding, may also be present provided that they too, in the amounts and under the conditions used, do not supply ingredients which would adversely affect the hardened case being formed. Normally, however, it is desirable to avoid such gases.

Finally, diluents such as helium, argon, the other inert gases, and any other gas which does not react under the conditions encountered during nitriding, can also be present.

From the above, it can be seen that, except for N_2 and the inert gases, essentially all of the gases that might be used to carry out the inventive process contain additional elements over and above the nitrogen and carbon atoms used for case hardening. Many of these additional elements can form unwanted compounds under certain circumstances, which could adversely affect the case being formed. For example, the hydrogen in methane can readily diffuse into titanium metal where it can form titanium hydrides under certain conditions. Similarly, the oxygen found in carbon dioxide and monoxide is known to cause a brittle case to form when titanium is nitrided. Similarly, carbon can form titanium carbide precipitates, which would reduce corrosion resistance. In carrying out the inventive process, therefore, care must be taken to avoid conditions of concentrations, temperature, etc. which would lead to such unwanted compounds. This can easily be determined by routine experimentation and reference to the literature, inasmuch as the conditions under which many of these unwanted compounds form are largely known.

The amounts of carbon-containing gas and nitrogen-containing gas (i.e. the "active gases") in the nitriding gas of the present invention can vary widely, and essentially any amounts can be used. Thus, the nitriding gas can be composed solely of the active gases, if desired. Alternatively, the active gases can form only a small part of the nitriding gas, with the vast

majority of the nitriding gas being composed of an inert gas and/or a complementary reactant gas. For example, the active gases can be as little as 1% of the nitriding gas, with concentrations on the order of 1 to 10%, or 2 to 5%, being typical. Larger concentrations of the active gases, e.g. at least 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90% and 95%, for example, can also be used. Thus, it has been found convenient to use nitriding gases in which the amount of nitrogen-containing gas, and especially nitrogen, is at least about 50 mol.%, more typically at least about 65 mol.% or even 75 mol.% or more, while the amount of carbon-containing gas is about 5 to 40 mol.%, more typically about 10 to 15 mol.%. However, as shown in the working examples below, nitriding gases containing as little as 1% nitrogen and 2% carbon-containing gas can also be used.

The relative amounts of the carbon-containing and nitrogen-containing gases used in the present invention can also vary widely. Generally, these gases can be used in amounts such that the atomic ratio of nitrogen atoms to carbon atoms in nitriding gas (the "N/C ratio") will be about 20:1 to 1:20, more typically about 5:1 to 1:5, more typically about 2:1 to 1:2.

Nitriding Conditions

In prior technology as described in the above-noted patents, conventional nitriding of titanium can be accomplished at temperatures as low as 200° C and as high as 1200° C. However, as further pointed out in the above-noted Shetty et al. Patent, nitriding is normally carried out below about 880° C so as to avoid the heat distortion temperature of titanium (882° C) and above about 700° C so that the protective titanium oxide layer depassivates significantly so that nitridization can occur at a practical, commercially-feasible rate.

In accordance with the present invention, nitridization is also carried out at temperatures above about 700° C. This enables nitridization to proceed with the protective titanium oxide layer on the workpiece surfaces being significantly depassivated which, in turn, enables nitridization to occur at a significant rate for forming a deeper case than possible at slower rates. With respect to the maximum nitridization temperature, however, temperatures exceeding about 850° C should be avoided. This is because formation of titanium nitride cannot be avoided, as a practical matter, above these temperatures, even when methane or other carbon-containing gas is included in the system. Accordingly, nitridization will normally be accomplished in accordance with the present invention at temperatures of about 700° C to 850° C, more typically about 750 to 850° C, or even 800 to 840° C.

For example, it has been found in accordance with the present invention, that a titanium workpiece which is nitrided with a nitriding gas composed of 85% nitrogen and 15% methane at 800° C (for 90 hours) exhibits essentially no titanium nitride precipitates as reflected by the fact

that the corrosion resistance of its surface in 0.5% aqueous hydrofluoric acid is greater than the corrosion resistance of the titanium metal from which the workpiece is made.

In particular embodiments of the invention, it has been found that nitriding at 1 atmosphere pressure using 85% N₂ and 15% CH₄, as the nitriding gas at 700 to 800° C for 90 hours is effective. In particular, it has been found that nitriding pure titanium metal as well as titanium alloys such as Titanium 64 under these conditions produces case hardened surfaces 40 or more microns thick having outer hardnesses of 800 Vickers or more and corrosion resistances better than the base metal being nitrided, i.e. better than the corrosion resistance of the untreated metal from which the workpiece is made. These cases are as good as or even better than the cases produced by prior art nitriding processes in terms of thickness, hardness and corrosion resistance.

Other nitriding conditions can also be used. In addition, nitriding can be carried out to provide case hardened layers of less thickness (e.g. ≥35 microns, ≥30 microns, ≥25 microns, ≥20 microns, ≥15 microns, ≥10 microns or even ≥5 microns) and/or less hardness (e.g. ≥750 Vickers, ≥700 Vickers, ≥650 Vickers, ≥600 Vickers, ≥550 Vickers), as desired. Regardless of the particular target thickness and hardness desired, and regardless of the particular titanium alloy used, hardened cases of superior corrosion resistance will be achieved so long as the particular nitriding conditions used are selected in the manner described above.

Titanium Nitride Surface Layer

Analysis of case hardened workpieces produced by the present invention shows that a very thin surface layer of titanium nitrides may be formed on the nitride-free, case hardened layer produced by the present invention. This nitride surface layer may be as much as 2 microns thick but is usually much thinner, i.e., ≤1.5 microns, ≤1.0 microns, and even ≤0.5 microns. In general, the thickness of this outer layer is less than about 10%, more typically less than about 5% and even less than about 3% of the thickness of the nitride-free, case hardened layer produced by the present invention. This is much thinner than the titanium nitride-containing surface layers produced by conventional nitriding, which as indicated above are typically 5 to 20 microns thick or more.

The corrosion resistance of the nitride-containing surface layer produced by the present invention, as measured by contact with 0.5% aqueous HF, is unclear as of this writing. It is clear, however, that the corrosion resistance of the nitride-free hardened case produced by the present invention is superior to that of the base metal from which the workpiece is made. This is due at least in part, it is believed, to the essentially complete absence of titanium nitrides and carbides from this layer. In any event, because the nitride-containing surface layer produced by the

present invention is so thin while the nitride-free, hardened case layer produced by the present invention is so thick, the corrosion resistance of workpieces produced by the present invention as a whole are vastly superior to the corrosion resistance of workpieces produced by conventional nitriding and as good as and often better than the corrosion resistance of untreated metal.

In the same way, the fatigue strength of workpieces produced by the present invention compare quite favorably to the fatigue strength of similar workpieces which are either untreated or nitrided by conventional technology. As indicated above, the fatigue strength of workpieces nitrided by conventional technology can decrease by as much as a factor of seven and, in general, are at least 40% less than those of untreated workpieces. This is because the relatively thick, roughened surfaces produced by conventional nitriding introduce crack propagation sites into the workpiece surfaces. In the present invention, however, the nitride surface layer is so thin that effect of this roughened surface in terms of crack initiation is minimal. Thus, workpieces produced by the present invention can have fatigue strengths, although less than otherwise identical workpieces which are untreated, are still better than the fatigue strengths of conventionally nitrided workpieces of the same hardness. Indeed, some workpieces produced by the present invention have fatigue strengths as good as or even better than that of otherwise identical but untreated workpieces.

Underlayment Layer

In accordance with still another embodiment of the invention, it has been found possible to provide a case hardened surface with a dual layer construction in which the hardened case of the present invention is underlayed with an iron-containing foundation layer having an α/β duplex phases structure.

In accordance with this aspect of the invention, the titanium workpiece is provided with an iron coating prior to the nitriding process. This can be most easily be done by electroplating the workpiece with iron in accordance with conventional electroplating techniques. Alternatively, the iron coating can be applied by any other technique capable of providing a metal coating on a metal substrate. Examples are vapor deposition, sputtering and the like. Coating thickness of 0.3 to 1.5 microns, more particularly 0.9 to 1.2 microns, are appropriate.

Once the workpiece is coated with iron in accordance with this aspect of the invention, it can then be subjected to nitriding in accordance with the procedure described above. When this occurs, the iron on the workpiece surfaces appears to diffuse substitutionally into the body of the workpiece ahead of the nitrogen from the nitriding process where it deposits in the form of a discrete underlayment layer. In any event, the product formed in this aspect of the invention is composed of the body of the workpiece whose metal composition is unchanged, a hardened case

layer of the same composition and thickness described above and an iron-containing intermediate layer which exhibits an α/β duplex phases structure and in which some of the titanium atoms in the metal lattice have been replaced by iron atoms. In addition to iron, other "foundation metals" such as nickel which will substitutionally diffuse into α -phase titanium to form an α/β duplex phase structure may be used for this purpose.

WORKING EXAMPLES

In order to more thoroughly define the present invention, the following working examples are provided.

Example 1

A titanium disc made from Titanium 64 (Grade 5) and measuring 0.75 inch in diameter and 0.08 inch thick was subjected to nitriding by contact with a nitriding gas composed of 2.0% methane, 1.0% N₂ and 97% argon at 840° C for 45 hours. The nitrided product was removed from the furnace and allowed to cool to room temperature.

The workpiece was then sectioned to reveal a cross-section face and the hardness of metal forming the cross-sectional face, at discrete locations from its outside surfaces, was measured by Zeiss Hardness Tester to develop a hardness profile. The results are shown in Figure 1. Moreover, a photomicrograph of this cross-sectional face is shown in Figure 2.

An elemental analysis of the metal forming the cross-sectional face, at discrete locations from its outside surfaces, was determined by glow-discharge optical omission spectroscopy. The results are set forth Figure 3.

As can be seen from these figures, a hardened case over 40 microns thick was obtained.

Although only a few embodiments of the present invention have been described above, it should be appreciated that many modifications can be made without departing from the spirit and scope of the invention. All such modifications are intended to be included within the scope of the present invention, which is to be limited only by the following claims.

We claim:

1. A process for case hardening a metal workpiece made from titanium or titanium alloy comprising contacting the workpiece with a nitriding gas composed of a nitrogen-containing gas and a carbon-containing gas at a temperature of about 700 to 850° C for a time sufficient to form a hardened case at least about 5 microns thick and being essentially free of titanium nitride.
2. The process of claim 1, wherein enough of the metal forming the workpiece has an α -phase structure so that the resistance of the case hardened surface to corrosion by 0.5 wt.% aqueous hydrofluoric acid is greater than that of the metal forming the workpiece.
3. The process of claim 2, wherein at least 30% of the metal forming the workpiece has an α -phase structure.
4. The process of claim 1, wherein the workpiece is contacted with a nitriding gas at a temperature of about 750 to 850° C.
5. The process of claim 4, wherein the temperature is about 800 to 840° C.
6. The process of claim 4, wherein the nitriding gas contains N₂ and methane.
7. The process of claim 4, wherein the N/C atomic ratio in the nitriding gas is about 20:1 to 1:20.
8. The process of claim 7, wherein the N/C atomic ratio in the nitriding gas is about 5:1 to 1:5.
9. The process of claim 8, wherein the carbon-containing gas is methane.
10. The process of claim 1, wherein the metal is essentially pure titanium metal.
11. The process of claim 1, wherein the metal is a titanium alloy containing at least about 90 wt.% titanium.
12. The process of claim 1, further comprising coating the surfaces of the workpiece to be case hardened with a foundation metal capable of substitutionally diffusing into α -phase titanium to form an α/β duplex phase structure prior to nitriding so that the workpiece obtained by nitriding includes an underlayment layer between the body of the workpiece and its case hardened surface.
13. The process of claim 12, wherein the foundation metal is iron.
14. A titanium alloy workpiece having a hardened case at least about 5 microns thick, the hardened case being essentially free of titanium nitride and having a resistance to corrosion by 0.5% aqueous hydrofluoric acid greater than that of the metal from which the workpiece is made.

15. The workpiece of claim 14, wherein at least 30% of the metal forming the workpiece has an α -phase structure.

16. The workpiece of claim 15, wherein the metal is essentially pure titanium metal.

17. The workpiece of claim 15, wherein the metal is a titanium alloy containing at least about 90 wt.% titanium.

18. The workpiece of claim 14, wherein the workpiece includes an underlayment layer between the body of the workpiece and its case hardened surface, the underlayment layer containing a foundation metal and exhibiting an α/β duplex phase structure.

19. The workpiece of claim 14, wherein the foundation metal is Fe or Ni.

20. The workpiece of claim 19, wherein the foundation metal is iron.

21. The workpiece of claim 14, wherein the a hardened case at least about 10 microns thick.

22. The workpiece of claim 14, wherein the a hardened case at least about 20 microns thick.

23. The workpiece of claim 14 further comprising an outer titanium nitride surface layer 2.0 microns or less in thickness.

24. A process for minimizing the thickness of an outer titanium nitride surface layer which forms when titanium metal or an alloy of titanium metal is contacted with a nitriding gas composed of a nitrogen-containing gas at a temperature of 700° C or more, the process comprising including in the nitriding gas a carbon-containing gas.

25. The process of claim 24, wherein the temperature is about 700 to 850° C.

26. The process of claim 25, wherein the carbon-containing gas is methane, ethane or propane.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

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

PAJ, EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 05, 31 May 1999 (1999-05-31) & JP 11 043760 A (CITIZEN WATCH CO LTD), 16 February 1999 (1999-02-16) abstract	1, 14, 24
A		4, 5, 10, 11, 16, 17, 25
Y	CH 585 278 A (WERNER GÖHRING) 15 July 1977 (1977-07-15) column 1 -column 4	1, 14, 24
A		6-9, 26
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 02, 26 February 1999 (1999-02-26) & JP 10 306365 A (CITIZEN WATCH CO LTD), 17 November 1998 (1998-11-17) abstract ----	1,14,24
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