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(54) Case hardening titanium and its alloys

(57) An article of titanium or a titanium-based alloy is case hardened by heat treatment at a temperate of 750°C to 850°C and at a pressure in the order of atmospheric pressure in a diffusion atmosphere. The diffusion atmosphere comprises a carrier gas such as argon which does not react chemically with the article the said temperature range and carbon monoxide. The concentration of carbon monoxide in the oxygen diffusion atmosphere is in the range of 20 volumes per million to 400 volumes per million.

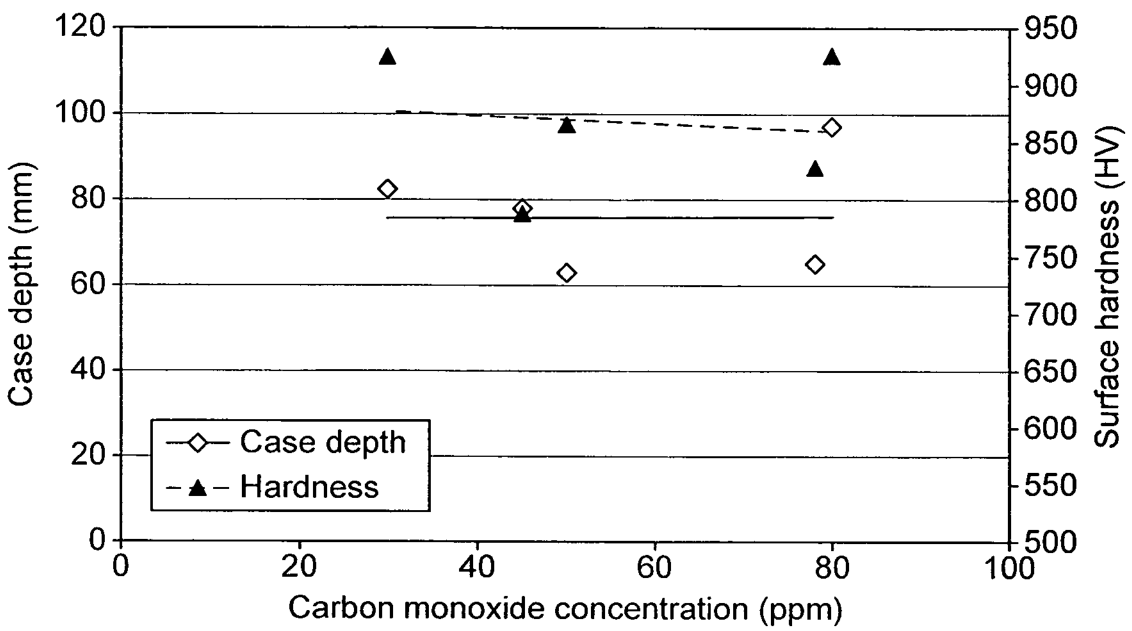

FIG. 1

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Description

[0001] This invention relates to a thermal treatment method. In particular, it relates to a method of case hardening an article of titanium or of an alloy based on titanium.

[0002] Titanium has poor tribological properties. Various coatings can used, for example titanium nitride, to improve the technological properties of the metal and its alloys but even so, their use in engineering is limited by the low strength of the substrate. Accordingly thermochemical diffusion treatments have been developed. To produce to a layer that is sufficiently thick to support a load in a reasonable time, oxidising and nitriding treatments are preferred at 965°C and 1050°C respectively. These high treatment temperatures degrade the core properties of the metal or alloy to such an extent that a further heat treatment becomes necessary after the formation of the case.

[0003] The state of the art is illustrated by the following documents.

[0004] WO-A-96/23908 discloses a process for manufacturing a titanium article with a hardened surface for enhanced wear resistance comprising the steps of exposing the article to an oxygen-containing environment; heating the article to a temperature that allows oxygen to diffuse into the article; soaking the article at the temperature for a time sufficient to oxidise elemental metal at the surface and cooling the article to room temperature. The heating and soaking take place at about 500°C, and the oxygen-containing environment is an atmosphere of air.

[0005] US-A-5 316 594 relates to forming a hardened outer shell on a refractory titanium workpiece using an argon-oxygen atmosphere containing from 1 to 3 mole percent of oxygen at a maximum treatment temperature of 815°C.

[0006] EP-A-580 081 relates to the treatment of intermetallic compounds of titanium and aluminium in an atmosphere containing 20% by volume of oxygen.

[0007] US-A-4 263 060 relates to the treatment of titanium articles with oxygen at a subatmospheric pressure.

[0008] WO-A-99/04055 (The University of Birmingham) discusses the need to provide engineering alloys of titanium or zirconium with a hard case consisting of a region of relatively high hardness maintained to a certain depth below the surface before dropping more steeply and then gradually to the hardness of the untreated core material. WO-A-99104055 discloses a method of case hardening an article formed of titanium, zirconium or an alloy of titanium and/or zirconium in which the article is heat treated for a short period of time, typically from 0.3 to 0.6 hour, in an oxidising atmosphere containing both oxygen and nitrogen (typically air) at a temperature in the range of 700 to 1000°C so as to form an oxide layer on the article, and then further heat treating the article in a vacuum or in a neutral or an inert atmosphere at a temperature in the range of 700 to 1000°C so as to cause oxygen from the oxide layer to diffuse into the article.

[0009] According to WO-A-99-04055 the case hardened article may then be surface treated by the method according to WO-A-98/02595 (The University of Birmingham) so as to improve the tribological behaviour of the article. This surface treatment comprises gaseous oxidation of the article at a temperature in the range of 500 to 725°C for 0.1 to 100 hours, the temperature and time being selected such as to produce an adherent surface component layer containing at least 50% by weight of oxides of titanium having a rutile structure and a thickness of 0.2 to 2 μm on a solid solution-strengthened diffusion zone wherein the diffusing element is oxygen and the diffusion zone has a depth of 5 to 50 μm.

[0010] The dual step oxidation/diffusion treatment of the method according to WO-A-99/04055 is difficult to control. A small variation in the amount of oxide formed in the first oxidation step can result in a significant difference in the eventual hardness profile at the end of the diffusion time in the vacuum or the neutral or inert atmosphere. The method therefore relies entirely on empirical control, thereby causing difficulties if it is required to treat a range of articles of different shapes and sizes.

[0011] According to WO-A-2004/007788 there is provided a method of case hardening an article of titanium or a titanium-based alloy, or of zirconium or a zirconium-based alloy, wherein the article is heat treated at one or more temperatures in the range of 850°C to 900°C and at a pressure in the order of atmospheric pressure in an oxygen diffusion atmosphere comprising (a) a carrier gas which does not react chemically with the article in the said temperature range and (b) molecular oxygen, wherein the concentration of oxygen in the oxygen diffusion atmosphere is in the range of 10 volumes per million to 400 volumes per million.

[0012] The method according to WO-A-2004/007788 is an improvement over prior methods because it enables a hard case to be formed in a single treatment step at atmospheric pressure and is easy to control. In order to optimise the method according to WO-A-2004/007788 a balance has to be struck between the temperature at which the work is subjected to the oxygen diffusion atmosphere and the duration of the treatment. In general, temperatures in the order of 900°C favour shorter treatment times than temperatures in the order of 800°C. We have discovered however, that at temperatures in the order of 900 °C, some undesirable microstructural coarsening of the grains within the work takes place. It is thus undesirable to exceed a temperature much above 850 °C. At 850 °C, we have found that total duration of the period of time throughout which the work needs to be exposed to the oxygen diffusion for a case of adequate thickness of some industrial uses can be unacceptably long and typically over 24 hours.

[0013] It is therefore an aim of the present invention to provide an alternative method that is capable of ameliorating the above described difficulty when treating an article of titanium or an alloy based on titanium.

[0014] According to the present invention there is provided a method of case hardening an article of a metallic material selected from titanium and titanium - based alloys, wherein the article is heat treated at a pressure in the range of 0.5 to 2 bar and a temperature in the range of 750 to 870 °C in a diffusion atmosphere comprising (a) carrier gas which does not react chemically with the article in the said temperature range and (b) as active gas, wherein the concentration of the active gas in the diffusion atmosphere is in the range of 20 to 400 volumes per million, and wherein the active gas is carbon monoxide.

[0015] The carbon monoxide concentration in the diffusion atmosphere is preferably in the range of 30 to 100 volumes per million. Reducing the carbon monoxide concentration below 30 parts per million can increase the time it takes to form a hard case of given depth. Increasing the concentration of carbon monoxide above 100 volumes per million does not appear to increase significantly the rate of formation or the ultimate depth of the case but it does have the effect of increasing the depth of a ceramic layer formed on the surface of the work by virtue of the active gas. Concentrations of carbon monoxide above 400 parts per million can result in the formation of an impermeable surface layer that prevents the achievement of an adequate case depth.

[0016] A further advantage of the method according to the present invention is that a wear-resistant ceramic layer can be formed at the surface of the work. We have been able to form a uniform ceramic layer approximately 6 μm thick when subjecting a work piece of a titanium - based alloy containing 6% by weight of aluminium and 4% by weight of varadium as the sole alloying elements to an argon atmosphere containing 100 volumes per million of carbon monoxide for a period of 24 hours at a temperature of 850°C. Below this layer the upper 15 to 20 μm of the diffusion zone had a fine lamellar structure.

[0017] The term "titanium-based alloy" as used herein has its usual meaning. That is an alloy containing more than 50% by weight of titanium. Typical alloying elements for use in titanium-based alloys include vanadium and aluminium.

[0018] The carrier gas is preferably a noble gas such as helium, xenon, neon or argon, or a mixture of one or more such noble gases. Argon is particularly preferred. Other gases may be included if they do not have any marked adverse affect on the required metallurgical engineering properties of the article. For example, traces of nitrogen at the parts per million level are typically found in commercially available argon and can be tolerated in the method according to the invention.

[0019] The method according to the invention is preferably performed at a pressure that is essentially the same as the prevailing atmospheric pressure, i.e. at a pressure in the range of 0.9 to 1.2 bar.

[0020] The duration of the heat treatment is preferably in the range of 12 to 24 hours.

[0021] The method according to the present invention is particularly useful in case hardening engineering components or other articles formed of commercially pure grades of titanium, of titanium-based alloys (α, $\alpha+\beta$, or β alloys).

[0022] When the article is required to have enhanced fatigue properties, it may be subjected after heat treatment to a mechanical surface treatment, such as shot peening.

[0023] The method according to the present invention will now be further described with reference to the following Examples and to the accompanying drawings, in which:

Figure 1 is a graph showing the Vickers hardness profile and case depth of first samples of titanium alloy at different carbon monoxide concentrations in case hardening treatment;

Figure 2 is a similar graph to Figure 1 but showing the relationship between case depth and diffusion temperature for a second sample of titanium alloy.

Figure 3 is a graph comparing the hardness profiles of specimens of titanium alloy treated in difference case hardening atmospheres:

Figure 4 is a graph comparing the dry wear properties of a specimen of a titanium alloy case hardened according to the invention with those of a case hardened steel.

Figure 5 is a graph comparing the dry wear properties of a specimen of a titanium alloy case hardened according to the invention with those of a case hardened steel.

Article 1. Examples

[0024] In the following examples, samples were treated in a small Boye pit furnace that had previously been used for carburising treatments. It was therefore thoroughly burnt out first, together with its loading jig, to ensure that no residues - particularly carbon - were present that might affect the results. This was done by passing carbon dioxide-free air through the furnace at 850°C for some hours while the carbon dioxide was monitored. Burnout was considered complete when the monitored carbon dioxide concentration began to fall.

[0025] The samples of the titanium-based alloy were in the form of polished cubes, 10mm per side. They were placed in the pit furnace at ambient temperature. The furnace was then heated under a flow or argon. When the processing temperature was reached, the processing gas mixture was introduced. At the end of the processing time the atmosphere was replaced by argon and the furnace cooled to below 150 °C before the samples were removed.

[0026] Because of the very small flow rate of addition gas(es) required, it proved impossible to achieve a stable addition gas concentration using pure addition gases and a Tylan General DynaMass Flow control system. Premixed cylinders of standard gases were therefore used to supply the addition gas to the mixer.

[0027] Preliminary screening runs at 850 °C for 24 hours to compare the method according to the invention (using carbon monoxide as the active gas) with that that according to WO-A-2004/007788 (using oxygen as the active gas) were performed. In addition, experiments were performed using carbon monoxide as the active gas and in supplementing the active gas with nitrogen gases or mixtures of gases containing oxygen, nitrogen and carbon indicated that carbon monoxide was found to be the most effective active gas. A range of addition levels, treatment temperatures and times was investigated. The composition of the near surface layers was analysed by x-ray diffraction.

[0028] The active gas level, as measured in the outlet stream, varied slightly during a given treatment so all the results below are experienced with reference to the average level over the treatment period.

Example 1

[0029] In this example, the effect of carbon monoxide in an argon diffusion atmosphere for treatments carried out at a temperature of 850 °C and at atmospheric pressure (1 bar) for 24 hours, was investigated. Results were obtained for different carbon monoxide concentration is in the range of 30 parts by volume (volumes) per million to 80 parts by volume per million are shown graphically in Figure 1. The case depth and hardness were measured by conventional methods. The depth of the case was deemed to be the thickness of the layer having a hardness above 400HV (Vickers Hardness).

[0030] It was observed that a sample treated at a carbon monoxide concentration of 78ppm had a distinct ceramic surface layer. Such a layer confers improved wear-resistance characteristics upon the case hardened article. No such layer was observed on the samples treated at a carbon monoxide concentration of 45ppm or less.

[0031] The observed variations in both the hardness and the case depth are within experimental error. Within the range of carbon monoxide concentrations investigated, the case depth and hardness did not vary much. Forming a ceramic layer is believed to be advantageous because it increases the wear resistance. Once the carbon monoxide concentration is high enough to form a ceramic layer on the surface, the underlying diffusion zone is unaffected by further increases in the carbon monoxide concentration in the treatment atmosphere. The thickness of the ceramic layer does however increase but this is believed not to be detrimental to at least some engineering applications even though the layer may be brittle.

Example 2

[0032] Samples were treated for 24 and 48 hours at 800°C using a carbon monoxide concentration of 55 volumes per million. The resultant case depths were 0.13 and 0.18mm respectively, This variation of case depth with time is exactly in agreement with that predicted by Fick's law.

Example 3

[0033] Samples were treated for 24 hours using a carbon monoxide concentration of 50 volumes per million and temperatures of 750°C, 800°C and 850°C in accordance with the invention, and 900 °C by way of comparison.

[0034] The resultant case depths obtained are shown graphically in Figure 2. Case depth is shown to increase with temperature. The results obtained were corrected for the small differences from the nominal 50 volumes per million carbon monoxide level in the measured carbon monoxide concentrations.

[0035] Another effect of the treatment is to tend to cause structural coarsening. Such coarsening was not significant for the treatment temperatures of 750 °C, 800 °C and 850 °C but was manifest in the samples treated at 900 °C. As a result the samples treated at 900 °C would have been unsuitable for many engineering uses because the structural coarsening inevitably lowers core strength. This would be particularly a problem for larger engineering components that require a deeper case than in the samples produced in accordance with this example.

Example 4

[0036] Test specimens of the T. - 6AL - 4V alloy were produced by heat treatment for 24 hours at 850 °C and atmospheric pressure in first a gas mixture of 50 parts by volume (volumes) per million of oxygen in argon, secondly 80 parts by volume (volumes) of carbon monoxide in argon, and thirdly 25 parts by volume carbon dioxide in argon. The concentrations were chosen to ensure that a thin ceramic surface layer was formed on each test specimen.

[0037] The treated specimens were subjected to dry wear tests on a pin-disc machine employing a stationary vertical bar and a rotary disc. The heat treated specimen is attached to the vertical bar and the disc rotated. The disc was made from a cold working tool steel hardened and tempered to 58RC. The disc brings a high pressure (approximately 4N/mm^2 to bear on the sample. Resultant marks on the sample were then analysed by methods well known in the art. The hardness of each specimen was also measured. The results obtained are shown graphically in Figures 3 and 4. Figure 3 shows that the carbon monoxide - treated samples had a significantly harder case than either the carbon dioxide - treated sample or the oxygen - treated sample. Figure 4 shows that the wear rate of the carbon monoxide-treated specimen is half that of the oxygen-treated specimen with the carbon dioxide treated specimen lying between them.

Example 6

[0038] The dry wear of a carbon monoxide treated specimen of Ti-Al6-V4 produced under the same conditions as the corresponding specimen of Figure 4 was compared to that of an optimally carburised steel (Mn20Cr5, carburised to 0.8% by weight carbon and a total case depth of 0.65mm, and direct oil quenched from 850 °C). The results are shown graphically in Figure 5. The wear is an order of magnitude less for the titanium specimen from the steel.

Claims

1. A method of case hardening an article of a metallic material selected from titanium, and titanium-based alloys, wherein the article is a heat treated at a pressure in the range of 0.5 to 2 bar and a temperature in the range of 750 °C to 870 °C in a diffusion atmosphere comprising (a) carrier gas which does not react chemically with the article in the said temperature range and (b) as active gas, wherein the concentration of the active gas in the diffusion atmosphere is in the range of 20 to 400 volumes per million, and wherein the active gas is carbon monoxide.

2. A method according to claim 1, wherein the carbon monoxide concentration in the diffusion atmosphere is in the range of 30 to 100 volumes per million.

3. A method according to claim or claim 2, wherein a wear-resistant ceramic layer is formed in the heat treatment at the surface of the article.

4. A method according to any one of the preceding claims, wherein the titanium-based allow is an alloy of titanium with 4% by weight of vanadium and 6% by weight of aluminium.

5. A method according to any one of the preceding claims, wherein the duration of the heat treatment is in the range of 12 to 24 hours.

6. A method according to any one of the preceding claims, wherein the article is an engineering component.

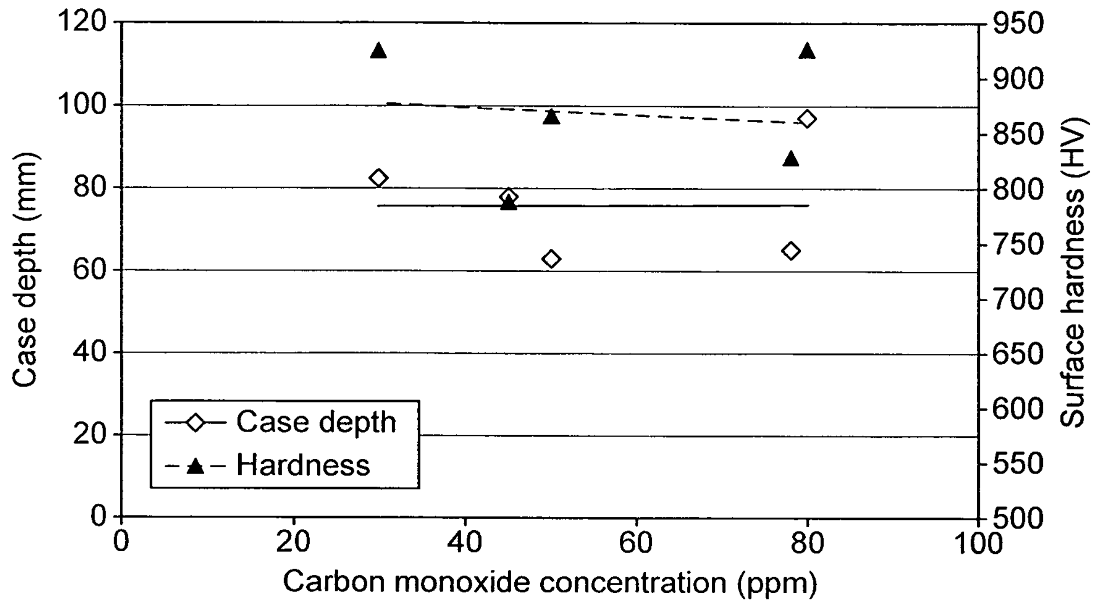
7. A method according to any one of the preceding claims, wherein the pressure is atmospheric pressure.

8. A method according to any one of the preceding claims, wherein the carrier gas is argon.

9. A method according to any one of the preceding claims, wherein the carrier gas is one or more of the following gases:

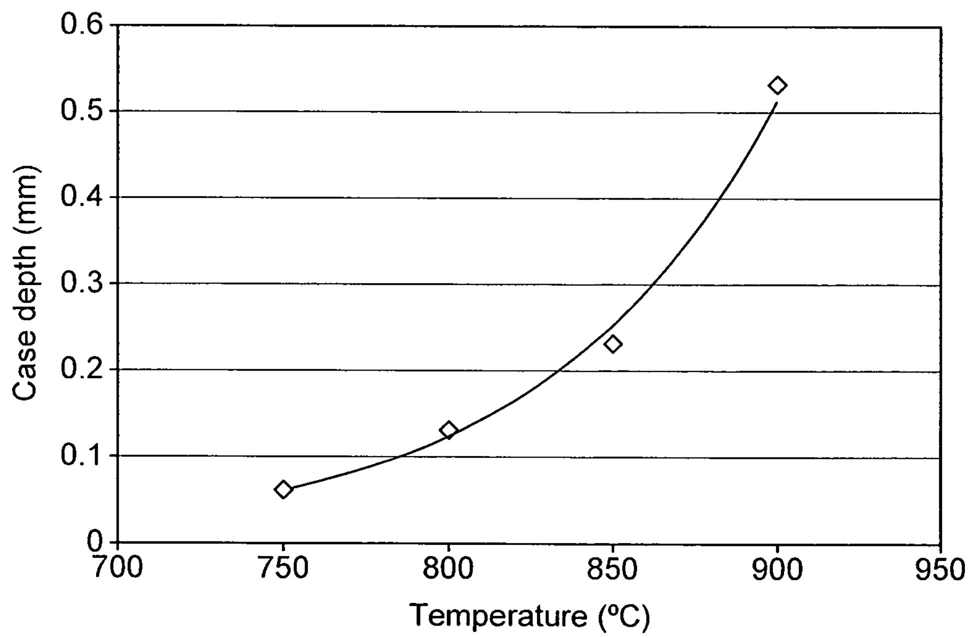
   helium, neon, krypton and xeon.

10. A method according to any one of the preceding claims, wherein the diffusion atmosphere is essentially free of molecular nitrogen.



120
100
80
60
40
20
0
950
900
850
800
750
700
650
600
550
500
0
20
40
60
80
100
Case depth (mm)
Surface hardness (HV)
Carbon monoxide concentration (ppm)
Case depth
Hardness

FIG. 1



0.6
0.5
0.4
0.3
0.2
0.1
0
700
750
800
850
900
950
Case depth (mm)
Temperature (ºC)

FIG. 2

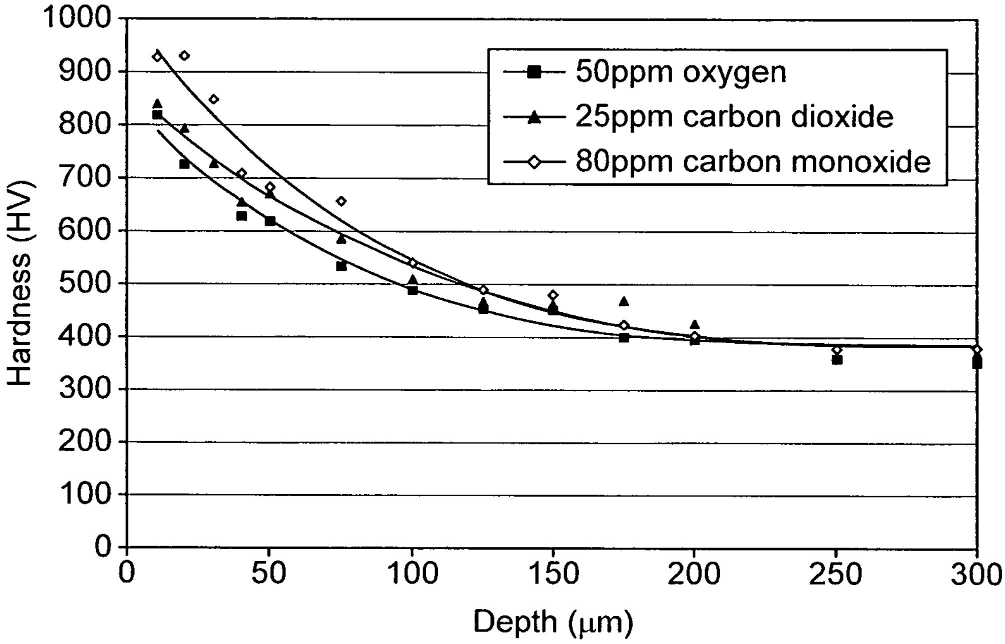

1000
900
800
700
600
500
400
300
200
100
0
Hardness (HV)
0
50
100
150
200
250
300
Depth (μm)
50ppm oxygen
25ppm carbon dioxide
80ppm carbon monoxide

FIG. 3

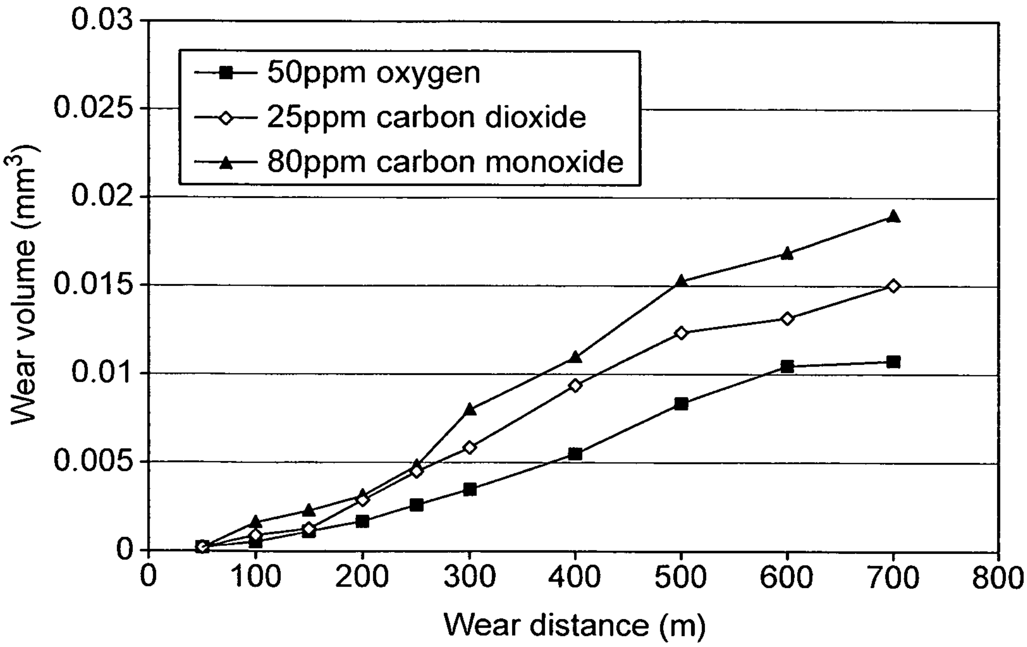

0.03
0.025
0.02
0.015
0.01
0.005
0
Wear volume (mm3)
0
100
200
300
400
500
600
700
800
Wear distance (m)
50ppm oxygen
25ppm carbon dioxide
80ppm carbon monoxide

FIG. 4

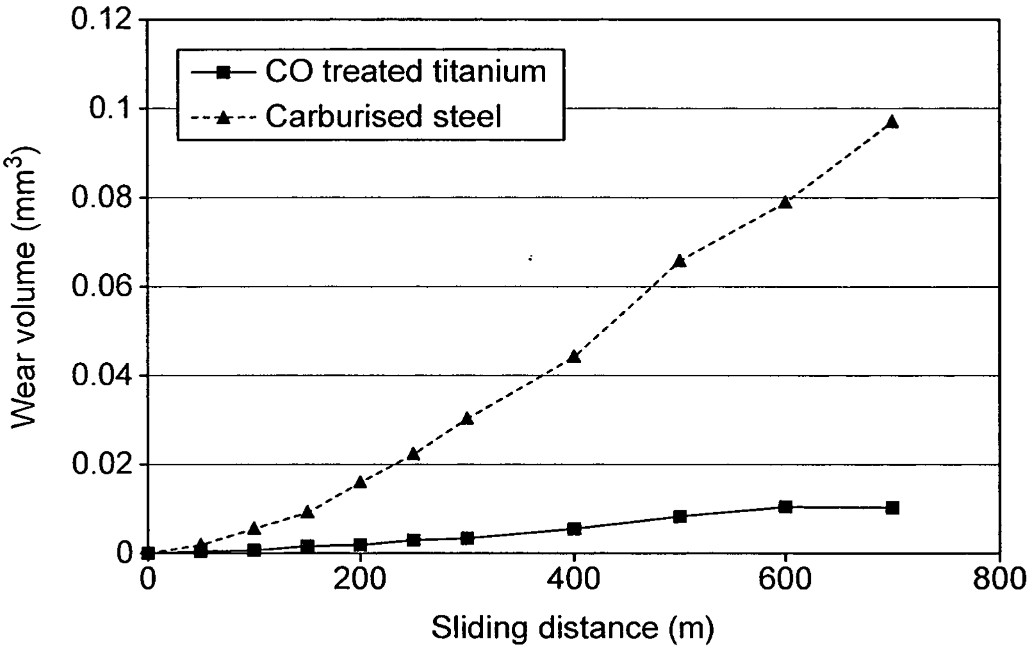

0.12
0.1
0.08
0.06
0.04
0.02
0
Wear volume (mm3)
CO treated titanium
Carburised steel
0
200
400
600
800
Sliding distance (m)

FIG. 5

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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	27 November 2009	Lilimpakis, Emmanuel

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EUROPEAN SEARCH REPORT

Application Number
EP 09 25 1856

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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