(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 288 328 A1

(12) # EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.03.2003 Bulletin 2003/10

(51) Int Cl.[7]: **C23C 8/16**, C23C 8/28
// F01L3/02

(21) Application number: **02290753.9**

(22) Date of filing: **27.03.2002**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **03.09.2001 JP 2001265462**

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(54) **Method for surface hardening a Ti alloy**

(57) Ti alloy is heated in an atmosphere of CO_2 in a heating furnace. O and C atoms are introduced into the Ti alloy to harden it without forming Ti oxide, thereby increasing hardness by Ti-O and Ti-C solid solutions thus formed.

EP 1 288 328 A1

Description

BACKGROUND OF THE INVENTION

[0001] This invention relates to a method of strengthening Ti alloy to improve wear resistance.

[0002] In automobile industries, poppet valves and other valve-operating parts are made of Ti alloy that provides high strength and low specific gravity. Poppet valves require wear resistance and scuff resistance at portion which is engaged with different valve-operating parts.

[0003] In order to strengthen Ti alloy material to provide wear resistance and scuff resistance, various methods have been developed. For example, oxides are formed on the surface of Ti alloy in Japanese Patent Pub. No.62-256956. Nitrides are formed on the surface in Japanese Patent Pub. No.61-81505. Carburizing is carried out to diffuse carbon atoms into Ti alloy in Japanese Patent No.2,909,361.

[0004] Wear resistance and scuff resistance in the foregoing methods are improved in Ti alloy material, but the surface is so hard that different parts to be engaged are likely to be attacked.

[0005] Japanese Patent Application No.2001-25415 discloses a Ti alloy poppet valve in which Ti-O and Ti-C solid solutions are formed, and a method of manufacturing a Ti alloy poppet valve, comprising the steps of heating the Ti alloy valve at temperature lower than beta transformation point in a plasma vacuum finance which contains oxygen less than stoichiometric amount for forming Ti oxides to diffuse O and C atoms to form O and C diffusion layer which comprises Ti-O and Ti-C solid solutions to strengthen a valve body.

[0006] To diffuse O and C atoms, in the presence of O_2 less than stoichiometric amount for forming titanium oxides, heat treatment is carried out at about 800°C. Glow discharge is made in the presence of a gas for ionized carburizing, or plasma carburizing is carried out while oxygen less than stoichiometric amount for forming titanium oxide is supplied. Oxygen/carbon diffusion layer thus obtained not only improves wear and scuff resistance, but also decreases attacking property to other members.

[0007] However, as mentioned above, heat treatment is carried out in the presence of oxygen in a plasma vacuum finance and ionizing carburizing is carried out by glow discharge, which is complicate. Furthermore, it is necessary to employ a vacuum discharge device and plasma power source in a plasma vacuum finance to increase cost.

SUMMARY OF THE INVENTION

[0008] In view of the disadvantages in the prior art, it is an object of the present invention to provide a method of strengthening Ti alloy to diffuse oxygen and carbon atoms without forming titanium oxide.

[0009] According to the present invention, there is provided a method of strengthening Ti alloy, comprising the step of heating the Ti alloy in an atmosphere of CO_2 at 600 to 900°C in a heating furnace to diffuse C and O atoms into the Ti alloy.

BRIEF DESRIPTION OF THE DRAWINGS

[0010] The features and advantages of the present invention will become more apparent from the following description with respect to appended drawings wherein:

Fig. 1 is a micrograph of Ti alloy treated by Example 1 of the present invention;
Fig. 2 is a graph that shows oxygen and carbon atom concentration of the Ti alloy material in Fig. 1;
Fig. 3 is a graph of hardness to depth of Ti alloy material in Fig. 1;
Fig. 4 is a micrograph of Ti alloy treated in Example 3 of the present invention;
Fig. 5 is a micrograph of Ti alloy treated in Comparative Example 2;
Fig. 6 is a graph of the results of wear test to Ti alloy materials; and
Fig. 7 is a schematic view of a device for the wear test.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0011] Heat treatment of the present invention will be described as below.

[0012] Ti alloys include alpha alloys such as Ti-5Al-2.5Sn; near-alpha alloys such as Ti-6Al-2Sn-4Zr-2Mo(hereinafter refer to "Ti6242") and Ti-8Al-Mo-V; alpha-beta alloys such as Ti-6Al-4V, Ti-6Al-6V-2Sn and Ti-6Al-2Sn-4Zr-6Mo; and beta alloys such as Ti-13V-11Cr-3Al and Ti-15Mo-5Zr-3Al. Ti6242 may be preferably used.

[0013] In heat treatment, Ti alloy is put in a heating furnace, and air in the furnace is purged by CO_2. It is heated in an atmosphere of CO_2 at 600 to 900°C, preferably 800 to 850°C.

[0014] Below 600°C, diffusion speed of carbon atoms is too slow, which is disadvantageous in cost. Above 900°C, oxide layer is formed and the temperature exceeds beta transformation point of Ti to change its configuration, which is not preferable.

[0015] In heat treatment, to supplement CO_2 consumed by introduction of C and O into Ti alloy and to maintain CO_2 atmosphere in the furnace, CO_2 may be always fed into the heating furnace. Feeding rate may be 0.5 to 3.0 l /min, preferably 1.0 to 2.5 l /min,

[0016] Time for treatment in CO_2 affects wear resistance or hardness, and may be preferably 1 to 3 hours. By the heat treatment, O and C atoms are diffused at depth of 25 to 50μ m from the surface, and surface hardness is HV 550 to 1000.

[0017] When a poppet valve in an internal combustion engine of an automobile is made of Ti alloy, suitable Vickers hardness is HV 700 to 850. The valve treated by the method of the present Invention not only provides wear and scuff resistance, but also improves attacking property to the other member.

Example 1

[0018] In a muffle furnace which has volume of 24 1, a poppet valve made of Ti6242 was put as sample and CO_2 was introduced to purge air. CO_2 was fed into the furnace at the flow rate of 1 1 /min and the sample was heated till 800°C and maintained at the temperature for two hours. Then, the valve was cooled to room temperature without contacting air. After cooling, the sample was taken out of the furnace and various tests were carried out.

[0019] Fig. 1 illustrates a micrograph of a section of the sample. As illustrated in the micrograph, O and C atoms were introduced at the depth.

[0020] Fig. 2 is a graph which shows averages of concentrations of O and C atoms measured at each depth by an electric-field-radiation-type Auger electronic spectrometer. In the graph, an axis of abscissa denotes depth (μ m) from the surface of the sample, and an axis of ordinate denotes concentration (atomic %) of O and C atoms. The unit of concentration "atomic %" means rate of O and C atoms with respect to analyzed total atoms. The graph shows oxygen and carbon atoms in the diffusion layer of the sample.

[0021] X-ray diffraction in X-ray microdiffraction device identifies TiC, but does not find titanium oxide. From the result, oxygen atoms do not combine with titanium, but remain as atoms. Carbon atoms partially combine with titanium to form TiC, but the remaining is diffused as carbon atoms.

[0022] Section hardness of the sample thus obtained was measured by a Micro-Vickers hardness tester of Shimazu Corp. Fig. 3 shows distribution of hardness. An axis of abscissa means depth (μ m) from the surface, and an axis of ordinate means hardness (HV) under 100gf. It shows improvement in hardness up to depth of 50 μm according to the method of the present invention.

[0023] Figs. 2 and 3 prove that existence of oxygen and carbon atoms contributes improvement in hardness of Ti alloy.

[0024] As shown in Fig. 3, surface hardness was HV 830.

Examples 2 to 9 and Comparative Examples 1 to 3

[0025] Surface treatment was carried out under different temperatures and time with respect to Ti6242, and the following Table shows the results.

Table

	Temperature (°C)	Time (h)	Surface Hardness (HV)	Oxide Layer
Example 2	750	3	570	none
3	800	0.5	630	none
4	710	50	680	none
5	800	1	710	none
6	800	1.5	790	none
7	800	3	870	none
8	850	1	930	none
9	850	2	960	none

Table (continued)

	Temperature (°C)	Time (h)	Surface Hardness (HV)	Oxide Layer
Comparative Example 1	850	55	1030	formed
2	900	1	980	formed
3	1000	0.5	1030	formed

[0026] In an atmosphere of CO_2, Ti6242 was heated at 710 to 850°C for 0.5 to 50 hours, so that O and C atoms were introduced into Ti alloy without forming oxide.

[0027] Fig. 4 illustrates a microgragh of a Ti alloy poppet valve treated in the Example 3, and O and C diffusion layer was formed.

[0028] A poppet valve is used in an internal combustion engine of an automobile and is subjected to severe condition such as high temperature. Such a valve requires hardness of HV 700 to 850. In Examples 1, 5 and 6, a sample requires to be subject to the conditions of time for 1 to 2 hours at 800°C.

[0029] As clarified in Comparative Example 1, the temperature 850°C was the same as those in Examples 8 and 9, but it took 55 hours to attain HV 1030. But it was so long that an oxide layer was formed on the surface. Deformation is large and it is not suitable.

[0030] In Comparative Examples 2 and 3, when the temperature was over 900°C, surface hardness was sufficient, but a thick oxide layer was formed to cause large deformation, which was not suitable for actual use.

[0031] Fig. 5 shows a micrograph of a poppet valve in Comparative Example 2, in which an oxide layer was formed on an O and C diffusion layer.

[0032] Fig. 6 illustrates results of wear tests of Ti6242 in Examples 1 and 3, Comparative Example 2, untreated Ti alloy and tuftriding-treated heat-resistant steel.

[0033] To carry out the test, as shown in Fig. 7, a test piece 2 is engaged in a valve guide 1 made of Fe-sintered material. Vertical weight "W" for 6kgf was loaded and the test piece 2 was reciprocally slid for 50 hours while lubricating oil was supplied between them.

[0034] The test piece made of untreated Ti6242 was the maximum in wear, and wear becomes smaller in order of Example 3, Example 1, heat-resistant steel and Comparative Example 2. Example 1 is equivalent to the heat-resistant steel in wear. Owing to difference in surface hardness, Example 3 is larger than Example 1 in wear. The minimum wear in Comparative Example 2 seems to be due to an oxide layer on the surface. Comparative Example 2 was too rigid, so that wear of the valve guide 1 engaged therewith was the maximum.

Claims

1. A method of strengthening Ti alloy, comprising the step of:

heating the Ti alloy in an atmosphere of CO_2 at 600 to 900°C in a heating furnace to diffuse C and O atoms into the Ti alloy.

2. A method as claimed in claim 1 wherein the method is carried out for 0.5 to 50 hours.

3. A method as claimed in claim 1 wherein the method is carried out at 800 to 850°C.

4. A method as claimed in claim 3 wherein the method is carried out for 1 to 3 hours.

5. A method as claimed in claim 1 wherein CO_2 is always introduced into the heating furnace.

6. A method as claimed in claim 1 wherein the method is carried out at about 800°C for 1 to 2 hours.

7. A method as claimed in claim 6 wherein the Ti alloy is used to make a poppet valve in an internal combustion engine.

FIG.1

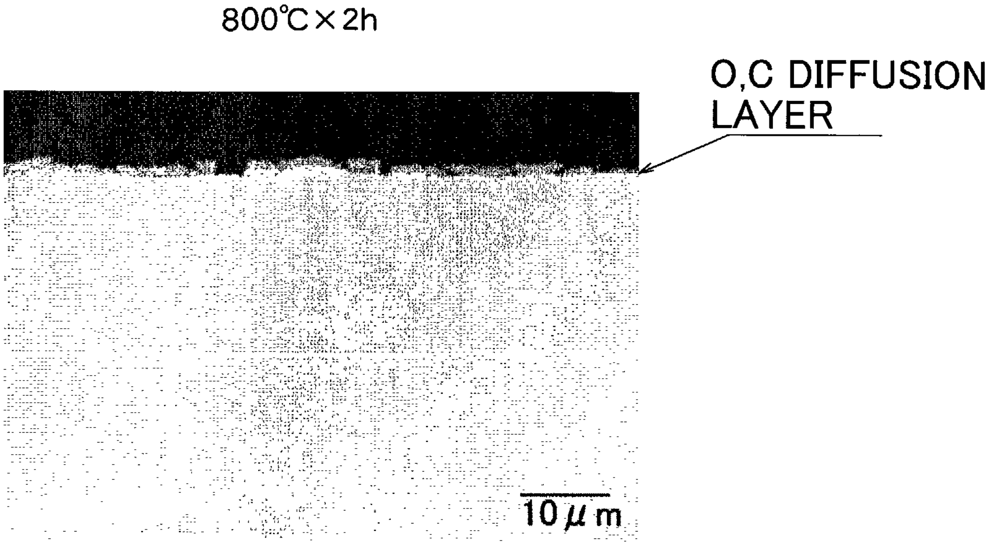

800℃×2h
O,C DIFFUSION LAYER
10 μm

FIG.2

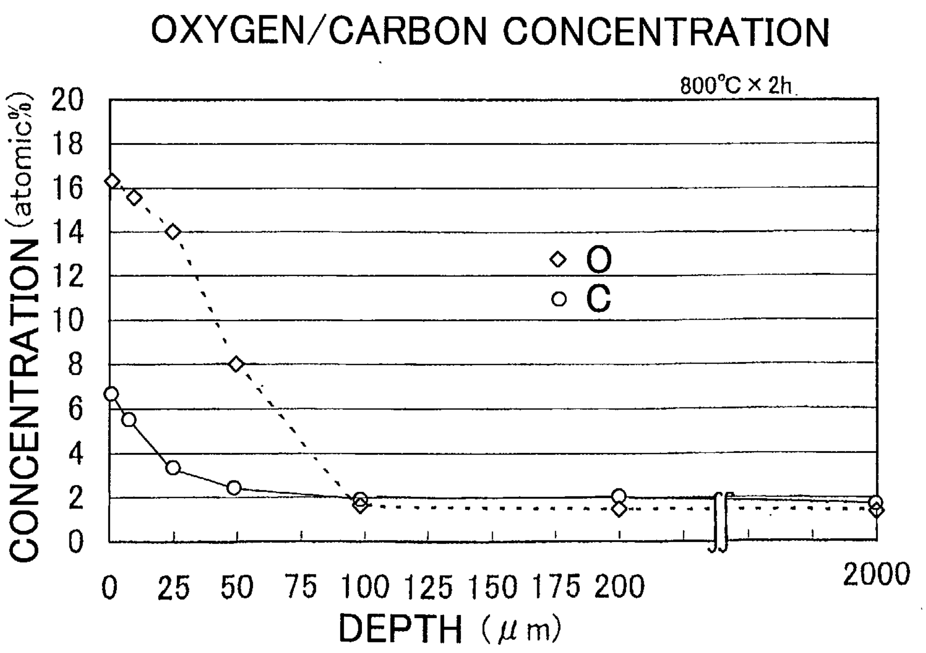

OXYGEN/CARBON CONCENTRATION
800℃×2h
CONCENTRATION (atomic%)
20
18
16
14
12
10
8
6
4
2
0
◇ O
○ C
0 25 50 75 100 125 150 175 200
2000
DEPTH (μm)

FIG.3

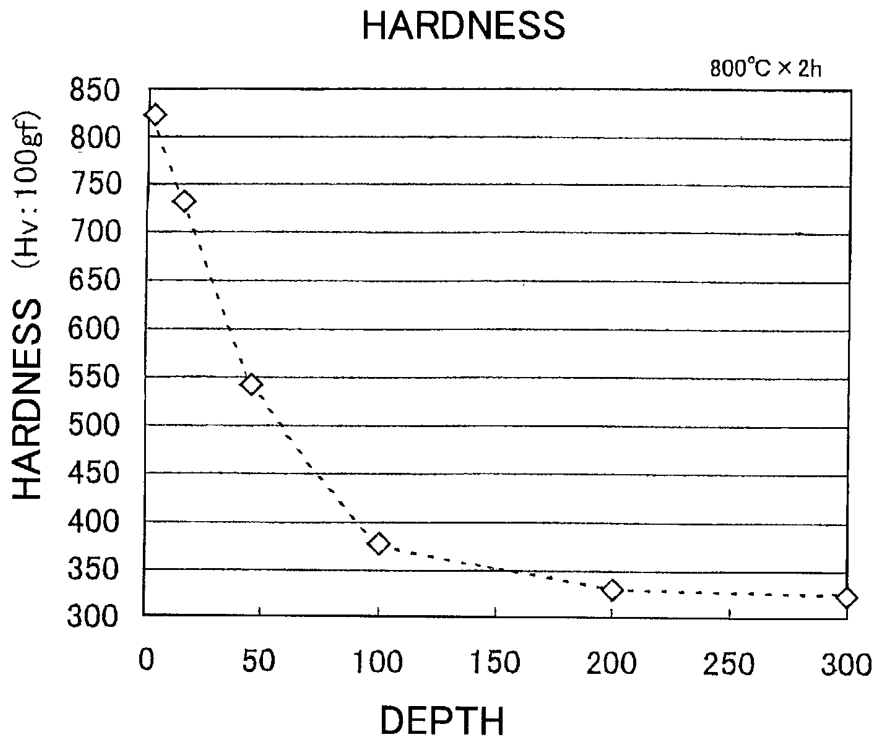

HARDNESS
800°C × 2h
HARDNESS (Hv:100gf)
850
800
750
700
650
600
550
500
450
400
350
300
0
50
100
150
200
250
300
DEPTH

FIG.4

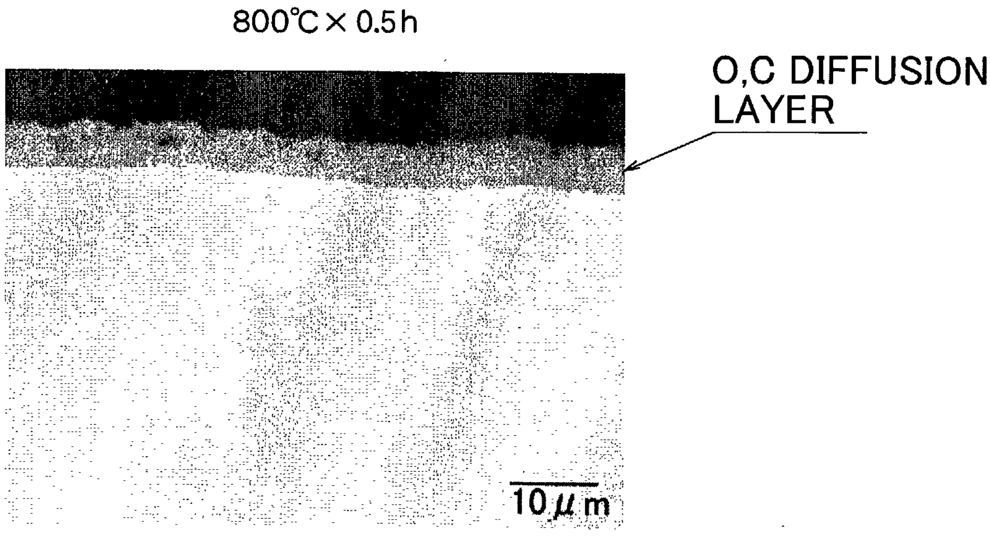

800°C × 0.5h
O,C DIFFUSION LAYER
10 μm

FIG.5

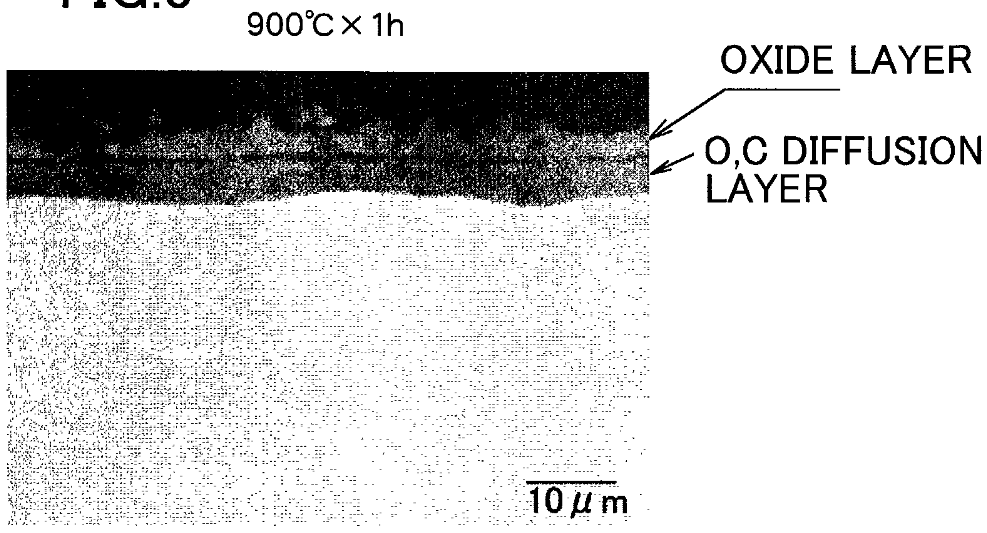


FIG.6

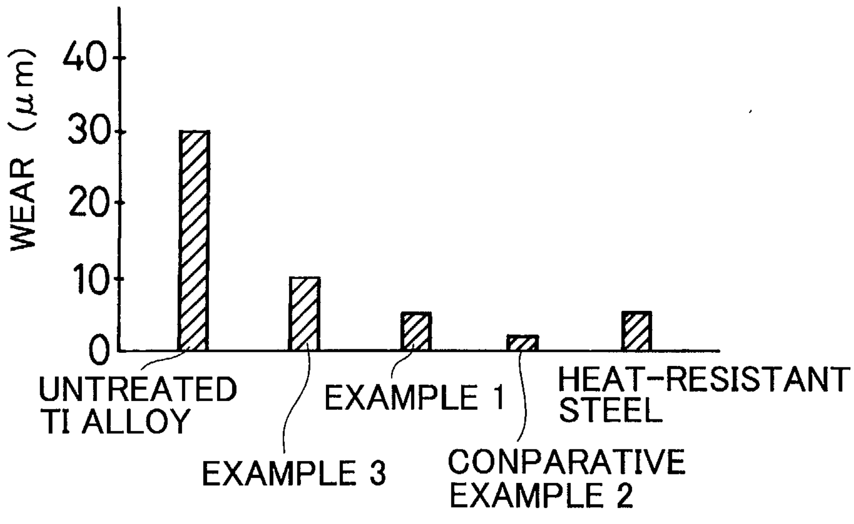
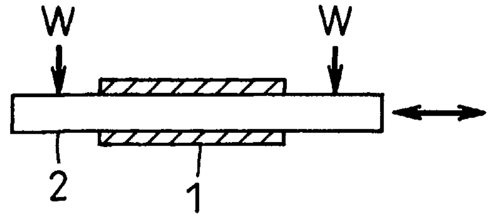


FIG.7



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EUROPEAN SEARCH REPORT

Application Number
EP 02 29 0753

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X Y	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 08, 30 August 1996 (1996-08-30) -& JP 08 104970 A (NKK CORP), 23 April 1996 (1996-04-23) * abstract * ---	1-6 1-7	C23C8/16 C23C8/28 //F01L3/02
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 07, 31 August 1995 (1995-08-31) -& JP 07 097676 A (NKK CORP), 11 April 1995 (1995-04-11) * abstract * ---	1-6	
Y	US 6 131 603 A (FUJI OOZX INC.) 17 October 2000 (2000-10-17) * claim 1 * -----	1-7	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	7 November 2002	Chebeleu, A

CATEGORY OF CITED DOCUMENTS

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07-11-2002

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