Surface Modification of Titanium using Laser Beam*

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Pure titanium has an excellent biocompatibility in comparison with stainless steels and Ti-Al-V alloys. We would expect pure titanium to have application for artificial joints and artificial bones if the wear resistance of the pure titanium were to be improved. So the surface modification of the pure titanium was performed using YAG laser beam. The laser power was 1.5 kW and Ar was used as the shielding gas. The shielding gas flow rate was changed from 5 to 40 L/min with a constant laser torch traveling speed of 500 mm/min. First, we investigated effects of the shielding gas flow rate on the Vickers hardness of the laser melted zone. When the shielding gas flow rate decrease, the average hardness increases and the oxygen and nitrogen concentrations of the laser melted zone also increase. We made clear the relationship between the average hardness and the nitrogen equivalent in the laser melted zone as follows. When the square root of the nitrogen equivalent ($N_{eq} = N + O/2$) was less than 0.1, a plot of the average hardness for the square root of the nitrogen equivalent reveals a linear relationship. However, the average hardness of the laser melted zone increased more than the value indicated by the linear relationship when the square root of the nitrogen equivalent was above 0.1. Next, metallurgical analyses of the laser melted zone were performed using an electron probe micro analyzer (EPMA), an X-ray diffraction method (XRD) and a transmission electron microscope (TEM), and effects of the behavior of oxygen and nitrogen on the hardness of the laser melted zone were studied. A uniform dislocation structures in the laser melted zone is observed over a wide area where there is the linear relationship between the hardness and the square root of the nitrogen equivalent. Lamellar structure, which alternated between two phases of α Ti and TiN in the laser melted zone, was formed where the hardness is greater than those indicated by the linear relationship. One phase of TiN contained a large quantity of nitrogen, and the other phase of α Ti contained little nitrogen. It is found that the lamellar structure composes of α Ti and Ti-nitrides (TiN and TiN_{0.26}). It is also observed that a wide area of α Ti possesses a twin structure with a high dislocation density.

(Received January 16, 2004; Accepted March 30, 2004)

Keywords: surface modification, titanium, laser, biocompatibility, Ti-nitride, lamellar structure

1. Introduction

Pure titanium has an excellent biocompatibility in comparison with stainless steels and Ti-Al-V alloys. We would expect pure titanium to have applications for artificial joints and artificial bones if the wear resistance of the pure titanium were to be improved. By means of an optical microscope, a serrate structure is observed in the laser melted zone, regardless of the laser irradiation conditions. As the Ar-shielding gas flow rate is decreased, the oxygen and nitrogen concentrations in the laser melted zone increase, and both the hardness and the tensile strength also increase. Furthermore, Okazaki *et al.*,^{1,2)} Conrad³⁾ and Tyson⁴⁾ reported on the relationship between the soluble oxygen and/or nitrogen concentrations in Ti-O alloys and Ti-N alloys and the hardness, the yield strength and the flow stress of the alloys.

To begin with, we investigated the effects of the Ar-shielding gas flow rate on the Vickers hardness of the laser melted zone. Then, the relationship between hardness and nitrogen equivalent in the laser melted zones was established, using the equation of Okazaki *et al.*²⁾ Next, metallurgical analyses of the laser melted zones were performed using an electron probe micro analyzer (EPMA), an X-ray diffraction method (XRD) and a transmission electron microscope (TEM), and the effects of the behavior of oxygen and nitrogen on the hardness of the laser melted zones were studied.

2. Experimental Procedures

The material used in this study was a commercial-pure titanium TP340C and the chemical composition is listed in Table 1. The thickness, width and length of the specimens were 2, 50 and 150 mm, respectively. The specimen surfaces were cleaned with acetone. Then, a length of 100 mm in the center of the specimens was melted using a YAG laser processor (Sumitomo Heavy Industries, MW2000). The focus of the laser beam (focal distance: 12.5 mm, spot diameter: 2 mm) was adjusted on the specimen surface, and then the laser torch was tilted by 10 degrees in the traveling direction. Table 2 shows the laser irradiation conditions. The laser power was 1.5 kW and Ar was used as the shielding gas. We investigated the effect of shielding gas flow rate on Vickers hardness of the laser melted zones when the

Table 1 Chemical composition of a titanium plate used (mass%).

Material	H	O	N	Fe	Ti
TP340C (t2)	0.0012	0.0487	0.0075	0.06	Bal.

Table 2 Laser irradiation conditions.

Laser power, <i>P</i> /kW	Traveling speed, <i>v</i> /mm·min ⁻¹	Shielding gas flow rate, /L·min ⁻¹
1.5	500	5, 10, 15, 20, 30 and 40

*This Paper was Presented at the Kyushu Branch Meeting of the Japan Institute of Metals, held in Kitakyushu, on June 6, 2003.

shielding gas flow rate was changed from 5 to 40 L/min with a constant laser torch traveling speed of 500 mm/min.

A cross section of the laser melted zone was polished to a mirror like finish and the hardness profiles were measured at a depth of 1.0 mm from the surface of the laser melted zone, using a micro Vickers hardness tester (load:0.49 N, time: 20 seconds).

Quantitative analyses of oxygen and nitrogen in the laser melted zones were performed using an oxygen and nitrogen simultaneous analysis equipment (LECO-TC136). The specimens used for gas analysis were cut out with approximate dimensions of 2 mm × 2 mm × 5 mm from the laser melted zones only and were polished using emery paper of # 100 in order to remove the oxide layer of the specimen surfaces.

High resolution microstructure observation of the laser melted zones was performed using both a TEM H-900NAR (acceleration voltage: 300 kV, selected area: ϕ 200 nm) and a TEM JEM-2010F (acceleration voltage: 200 kV, selected area: ϕ 140 nm). To produce specimens used for a TEM observation, disks having 3 mm diameter with a thickness of 150–200 μ m were cut parallel to the top surface of the laser melted zone; thereafter thin films were produced by mechanical grinding, dimpling and ion milling processes.

3. Results

3.1 Hardness Distribution of the Laser Melted Zone

Hardness distributions of the laser melted zones, produced using shielding gas with flow rates of 5 and 40 L/min, are shown in Fig. 1. The hardnesses of the laser melted zones rapidly increase in the laser melted zone boundary and are more than that of the base metal, about 150HV. Where the shielding gas flow rate of 5 and 40 L/min, the average hardnesses of the laser melted zones are about 450 and 210HV, respectively. The relationship between the average hardness of the laser melted zones and the shielding gas flow rate is shown in Fig. 2. When the shielding gas flow rate decreases, the hardness gradually increases. However, when

Fig. 1 Hardness distributions of laser melted zones protected with shielding gas flow rates of 5 and 40 L/min.

Fig. 2 Relationship between average hardness of laser melted zones and shielding gas flow rate.

Fig. 3 Relationship between nitrogen and/or oxygen concentrations of laser melted zones and shielding gas flow rate.

the shielding gas flow rate was less than 15 L/min, the hardness rapidly increases.

3.2 Effect of Shielding Gas Flow Rate on the Nitrogen and Oxygen Concentrations

The relationship between the nitrogen and/or oxygen concentrations of the laser melted zones and the shielding gas flow rate is shown in Fig. 3. The nitrogen and oxygen concentration of the base metal, as shown by the broken lines, were 75 and 487 ppm, respectively. When the shielding gas flow rate decrease from 40 to 20 L/min, the nitrogen and/or oxygen concentrations gradually increase and then rapidly increase down to 5 L/min. Thus, the laser melted zones are obliged to contain nitrogen and oxygen even if the shielding gas is used to protect and the hardness of the laser melted zones depends on the nitrogen and oxygen concentrations.

4. Discussions

4.1 Relationship between Hardness and Nitrogen Equivalent

The relationship between the hardness H and the average grain sizes d is given in eq. (1), from the relationship between the hardness H and the yield strength and the equation of Hall-Petch.

$$H = H_0 + K_H/d^{1/2} \quad (1)$$

Where, H_0 and K_H are constants. Okazaki *et al.* produced several kinds of Ti-N alloys and Ti-O alloys by the zone melting method and examined the effects of grain size and interstitial solute concentration on the hardness at room temperature.¹⁾ As a result, the relationships between H_0 and K_H and the square root of the interstitial solute concentration are given using eqs. (2)–(5), respectively.

$$\text{Ti-N alloys } H_0 = 64 + 1400 \cdot N^{1/2} \quad (2)$$

$$K_H = 1.15 + 38 \cdot N^{1/2} \quad (3)$$

$$\text{Ti-O alloys } H_0 = 64 + 1000 \cdot O^{1/2} \quad (4)$$

$$K_H = 1.15 + 27 \cdot O^{1/2} \quad (5)$$

Where, N ($= 0.09$ – 0.61 at %) and O ($= 0.25$ – 0.45 at %) are the nitrogen and oxygen concentrations (at %), respectively. The gradients in eqs. (2) and (3) are 1.4 times the gradients in eqs. (4) and (5); that is, the effect of the square root of the nitrogen concentration $N^{1/2}$ on H_0 and K_H is 1.4 times the effect of the square root of the oxygen concentration $O^{1/2}$. Similarly, Conrad reported that the effect of nitrogen was twice the effect of oxygen on the yield strength³⁾ and Tyson also reported that the effect of nitrogen was approximately twice the effect of oxygen on the flow stress at 0.2 % strain.⁴⁾ Therefore, H_0 and K_H are given by eqs. (7) and (8), using the nitrogen equivalent N_{eq} defined in eq. (6) for Ti-N-O alloy, and the effect of the nitrogen equivalent on the hardness was examined.

$$N_{eq} = N + O/2 \quad (6)$$

$$H_0 = 64 + 1400 \cdot N_{eq}^{1/2} \quad (N_{eq}^{1/2} = 0.03\text{--}0.078) \quad (7)$$

$$K_H = 1.15 + 38 \cdot N_{eq}^{1/2} \quad (N_{eq}^{1/2} = 0.03\text{--}0.078) \quad (8)$$

Figure 4 shows the relationship between the hardness and the square root of the nitrogen equivalent obtained in this study. Microstructures in laser melted zones had an apparent grain size of 50–100 μm . The thin solid and the broken lines in the figure represent calculated results obtained using eqs. (1), (6), (7) and (8) for grain sizes d of 50 and 100 μm , respectively. It is clear that the hardness increases linearly with an increase of the square root of the nitrogen equivalent. It is considered that the difference in the grain size has very little effect on the gradient of the straight line and the hardness is affected by the nitrogen equivalent more than by the grain size. The symbol $\bullet$ in the figure represents the measured results for the laser melted zones with the supply of shielding gas at various flow rates. In addition the symbol $\circ$ represents the base metal. When the square root of nitrogen equivalent is less than 0.1, the experimental results, as indicated by the dotted line in the figure, reveal a linear relationship between the average hardness of the laser melted

Fig. 4 Relationship between hardness and square root of nitrogen equivalent.

zones and the square root of the nitrogen equivalent. It is considered that the increase of the hardness in this region is caused by the solution of oxygen and nitrogen in the laser melted zones. However, when the laser melting was performed with conditions of shielding gas flow rates of 5 and 10 L/min, the average hardness of the laser melted zones increased more than the value indicated by the linear relationship. It is considered that this increase in the hardness is caused by the formation of the second phase, which is different from the parent phase.

4.2 Distribution of nitrogen and oxygen

Metallurgical analyses of the laser melted zones were performed using EPMA, XRD and TEM for two cases, the first where there is the linear relationship between the hardness and the nitrogen equivalent (shielding gas flow rate: 40 L/min) and the second where the hardness is greater than indicated by the linear relationship (shielding gas flow rate: 10 L/min).

Figures 5(a) and (b) show composition images and linear analysis results for titanium, nitrogen and oxygen in the laser melted zones protected with shielding gas flow rates of 40 and 10 L/min, respectively. In the case of a shielding gas flow rate of 40 L/min (Fig. 5(a)), segregation of nitrogen and oxygen cannot be observed. In the case of a shielding gas flow rate of 10 L/min (Fig. 5(b)), lamellar structures are observed within the crystal grain of the composition image and the nitrogen concentration is seen to enrich in the region where the titanium concentration is decreased.

Figures 6(a), (b) and (c) show the scanning electron microscope (SEM) image, the composition image and the result of EPMA plane analysis of a laser melted zone, different from the results shown in Fig. 5(b), protected with a shielding gas flow rate of 10 L/min. Nitrogen (yellow in Fig. 6(c)) is present in the dark regions in the SEM image and the composition image, and titanium (red in Fig. 6(c)) can be observed in the intermediate regions. Though a region where oxygen had segregated was also observed, correlation was not observed with the contrast of the composition image.

Fig. 5 Composition images and linear analysis results for titanium, nitrogen and oxygen in laser melted zones. (a) With a shielding gas flow rate of 40 L/min. (b) With a shielding gas flow rate of 10 L/min.

4.3 Change of lattice constant

Figure 7 shows XRD patterns obtained from the base metal and the laser melted zone protected with a shielding gas flow rate of 10 L/min. No intermetallic compounds were observed in either the base metal or the laser melted zone. However, profiles of XRD peaks obtained from several diffraction planes of the laser melted zone were synthesized. These were

Fig. 7 XRD pattern obtained from base metal and laser melted zone protected with a shielding gas flow rate of 10 L/min.

separated and the lattice constants measured with a high degree of precision. Figure 8 shows XRD patterns of the diffraction plane (1013) for a separated example. The results for the lattice constants are shown in Table 3. The laser melted zone consists of two phases; one phase has a lattice constant equal to that of the base metal and the other phase shows a lattice constant with an increased c axis length compared with that of the base metal.

Consequently, the lamellar structures formed in the laser melted zone protected with a shielding gas flow rate of 10 L/min, consist of two phases. One phase contains a large quantity of nitrogen, and the other contains little nitrogen.

4.4 Microstructure of the laser melted zone

Figures 9(a), (b) and (c) show a bright field image (BFI), a selected area diffraction pattern (SADP) and indexed result in the laser melted zones at a shielding gas flow rates of 40 L/

Fig. 6 Result of EPMA plane analysis of a laser melted zone different from that shown in Fig. 5(b). (a) SEM image. (b) Composition image. (c) EPMA plane analysis result.

Fig. 8 Peak separation of XRD profile for diffraction plane of $(10\bar{1}3)$.

Table 3 Results of lattice constants of α Ti obtained with shielding gas flow rates of 10 L/min.

Materials	a/nm	c/nm
Laser melted zone:1	0.2958	0.4730
Laser melted zone:2	0.2958	0.4700
Base metal	0.2955	0.4692

min, respectively. A uniform dislocation structure is observed over a wide area. The region having the uniform dislocation structure consists of mostly β Ti and a very small amount of α Ti.

Figure 10(a) shows a BFI of low magnification in the laser melted zones at a shielding gas flow rates of 10 L/min. A lamellar structure is observed which is an alternated structure between a dark contrast parent phase (α Ti) and a white contrast region of about 1 μm in width at intervals of about 3 μm . Firstly, the white contrast region was examined using TEM. Fig. 10(b) shows a BFI of the region near the white contrast region shown in Fig. 10(a). From analyses of the SADPs in the regions encircled “a”, “b” and “c” in the photograph, regions of a, b and c were identified as TiN, TiN and α Ti, respectively. It is noted here that the laser melted zone contains nitrogen and oxygen and TiN and TiO have the same crystal structure of NaCl and the almost same lattice constant.^{5,6)} From these facts, it is difficult to distinguish TiN from TiO. However, the laser melted zone reveals much higher concentration of nitrogen than that of oxygen (see Fig. 3). Furthermore, solubility limit of nitrogen is considerably less than that of oxygen,^{7,8)} suggesting that oxygen tends to be in α Ti in solid solution. Therefore, the revealed phase of the white contrast region is considered to be of TiN. The dark field images (DFI) obtained from the $(1\bar{1}1)\text{TiN}$ and $(3\bar{3}1)\text{TiN}$ spots (indicated by circles in the SADPs) are shown in Figs. 10(c) and (d), respectively. From these DFIs, it is revealed that TiN is a polycrystalline substance.

Fig. 9 Observation of laser melted zone protected with a shielding gas flow rate of 40 L/min using TEM. (a) BFI. (b) SADP. (c) Indexed results.

Figures 11(a) and (b) show a BFI and DFI respectively of a region different from that shown in Fig. 10. There is lamellar of α Ti and TiN (white contrast region of Fig. 11(b)) of about 200 nm in width. Figures 12(a) and (b) show a BFI and SADPs of a region different from those shown in Figs. 10 and 11. A phase of 200–500 nm wide is observed. Analyses of SADPs in the regions encircled “a1”, “a2” and “a3” in the BFI, make clear that regions of a1 and a3 are of intermetallic compounds $\text{TiN}_{0.26}$ and region of a2 is of parent phase (α Ti). Khidirov reported that the phase of $\text{TiN}_{0.26}$ has a space group of $P\bar{3}m1$ (hexagonal structure) and the lattice constants of “a” and “c” are 0.2956 and 0.4765 nm.⁹⁾ Referring their experimental and calculated result of X-ray intensities, the phase of regions “a1” and “a3” was identified as $\text{TiN}_{0.26}$. Figures 13(a) and (b) show a BFI and the indexed result of SADP in a region different from those shown in Figs. 10, 11 and 12. These are identified as α Ti, $\text{TiN}_{0.26}$ and TiN as shown in the indexed result. Consequently, it is clear that the white contrast phase is α Ti, including Ti-nitrides ($\text{TiN}_{0.26}$ and/or TiN).

Next, the black contrast phase shown in Fig. 10(a) was examined using TEM. Figures 14(a), (b) and (c) show a BFI, SADP and indexed result, respectively. A high strain field due to containing a large amount of dislocation is observed (Fig. 14(a)). Furthermore, extra spots are observed besides the fundamental spots of α Ti. The extra spot reveal at the

Fig. 10 Observation of laser melted zone protected with a shielding gas flow rate of 10 L/min using TEM. (a) BFI of low magnification. (b) BFI of region near the white contrast region shown in Fig. 10(a). (c) DFI obtained from $(1\bar{1}1)_{\text{TiN}}$ spot. (d) DFI obtained from $(3\bar{3}1)_{\text{TiN}}$ spot.

reciprocal lattice positions of $\pm 1/3(\mathbf{a}_1^* - \mathbf{a}_3^*)$ where the vector $(\mathbf{a}_1^* - \mathbf{a}_3^*)$ correspond to $(10\bar{1}0)\alpha\text{Ti}$ in the real space and the extra spots indicate the twin formation¹⁰⁾ (Figs. 14(b) and (c)). Thus the αTi contains a large amount of lattice defects.

As mentioned above, the lamellar structure is very complicated, but it is considered to bring about a marked rise in the hardness due to the fact that it consists of, at least, αTi with a high dislocation density and Ti-nitrides. Consequently, if the titanium surface is laser-melted, lamellar structures are formed in the surface layer of the titanium and the surface layer hardness is modified from approximately 400 to 500HV. So it is considered to improve the wear resistance of titanium.

5. Conclusions

We investigated, by means of metallurgical analyses, titanium melted zone protected with a YAG laser under different conditions of Ar-shielding gas flow rate. Main results obtained are as follows.

- (1) The average hardness of the laser melted zones increased linearly with the increase of the square root of the nitrogen equivalent and then increased more rapidly than the linear relationship.
- (2) A uniform dislocation structure in the laser melted zone with a shielding gas flow rate of 40 L/min, was observed using a TEM.
- (3) Lamellar structure, composed of two phases in the laser melted zone with a shielding gas flow rate of 10 L/min, was formed. One phase contained a large quantity of nitrogen, and the other phase contained little nitrogen.
- (4) The lamellar structure consisted of αTi and Ti-nitrides ($\text{TiN}_{0.26}$ and/or TiN) and a wide area of αTi exhibits a twin structure containing a high dislocation density. Consequently, by laser surface melting, the surface hardness of the pure titanium was modified to approximately 450HV.

Acknowledgments

Thanks are due to Mr. N. Wakayama, Center of Instrumental Analysis, Kyushu Institute of Technology, for his aids in this experiment.

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Fig. 11 Observation of a region different from that shown in Fig. 10 using TEM. (a) BFI. (b) DFI.

Fig. 13 Observation of a region different from those shown in Figs. 10, 11 and 12 using TEM. (a) BFI. (b) Indexed result.

Fig. 12 Observation of a region different from those shown in Figs. 10 and 11 using TEM. (a) BFI. (b) SADPs.

Fig. 14 Observation of region near the dark contrast region shown in Fig. 10(a) using TEM. (a) BFI. (b) SADP. (c) Indexed result.

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