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Surface Alloying of Titanium Using a Nanosecond Laser with a Light-Transmitting Resin

Takutoki Yamaiguchi and Hideiki Haginoi

Titanium and its alloys have several desirable qualities. They are very resistant to corrosion and have a high specific strength. However, their bad tribological qualities rule out using them on any moving components. When compared to more traditional methods of surface modification, laser alloying clearly stands out as a superior method for enhancing attributes like wear resistance. Unfortunately, the laser-alloyed zone is prone to developing flaws like fractures and voids, therefore the method isn't without its drawbacks. Our team has previously created a unique laser alloying technology that uses a light-transmitting resin as its carbon source. This method creates a laser-alloyed zone that is resistant to cracking. To reduce the total volume of molten metal and therefore increase process stability, a nanosecond pulsed laser was used for the laser alloying procedure in the current investigation. A smooth, defect-free laser-alloyed region was achieved. The laser-alloyed region included a high concentration of titanium oxycarbide particles. The laser-alloyed region exhibited a low friction coefficient and excellent wear resistance when in contact with the WC-Co ball.

Keywords: surface modification, wear resistance, laser alloying, light-transmitting resin, and titanium

1. Introduction

Titanium and its alloys have various excellent properties such as good corrosion resistance and high specific strength. However, they have not been applied to the sliding parts under sever wear condition due to their poor tribological properties [1]. Several surface-hardening treatments have been applied to improve the wear resistance of titanium. In applications with hard coatings such as PVD and CVD, poor adhesion strength between the coating layer and base metal often results in delamination [2]. In plasma carburizing treatments, the long treatment time at high temperature tends to coarsen the grain and cause heat distortion [3]. Laser surface alloying, an effective process for improving wear resistance, is performed by melting the surface of a substrate with added materials, mixing the components together, and rapidly solidifying the mixture [4]. The process attains the advantages of low thermal strain, fine microstructure, and flexibility in the choice of substrates and added materials [5]. Laser alloying can also be applied selectively to circumscribed areas of a treated product. Many studies have investigated the laser alloying of titanium for improving wear resistance. Several have attempted to improve the wear resistance through the *in- situ* synthesis of hard phases such as titanium nitride or titanium carbide through a laser alloying processes with nitrogen gas or carbon powder [6-10]. Laser alloying is flawed, however, as the brittleness of these hard phases often promotes the formation of cracks in the laser-alloyed zone. Earlier our group developed a novel laser alloying technique with a light-transmitting resin as a source for the carbon element using a CW fiber laser [11]. The technique. Ahigh peak power is available by using a nanosecond pulse laser, therefore a nanosecond laser might be able to melt the surface of substrate even though the total heat input is lower than that of a CW laser. In the present study we applied laser alloying treatment using a nanosecond pulse laser in an attempt to prevent damage to the resin layer by reducing the heat input and improve the surface integrity by minimizing the mass of the molten metal.

2. Experimental procedure

The specimens were cut into 25 mm × 25 mm squares from 5-mm-thick commercial pure titanium plates (grade

Osaka Research Institute of Industrial Science and Technology,
2-7-1, Ayumino, Izumi, Osaka 594-1157, Japan
E-mail: t_yamaiguchi@tri-osaka.jp

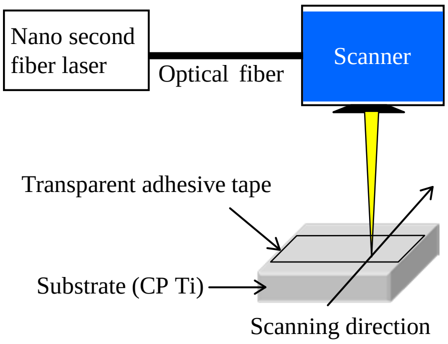

Fig. 1 Experimental setup.

Table1 Laser irradiation conditions.

Wave length	1064 nm
Pulse width	100 ns
Spot diameter	30 μm
Frequency	200 kHz
Average power	10 W
Scanning speed	100 mm/s
Scanning pitch	15 μm

2), polished with SiC paper (P400), and cleaned with acetone.

Before commencing the laser irradiation, a commercial transparent adhesive tape consisting of cellulose acetate film and acrylic adhesive (total thickness of about 50 μm) was laminated on the surface of the titanium specimen as a light-transmitting resin.

A nanosecond single-mode fiber laser (YLP-1-100-20-20) was focused to a spot diameter of 30 μm and scanned across the specimen surface with a galvano scanner. Fig. 1 and Table 1 show the experimental setup and laser alloying conditions, respectively.

The microstructure and chemical composition of the laser-alloyed zone were studied using an optical microscope (OM), scanning electron microscope (SEM), and electron probe microanalyses (EPMA). X-Ray diffraction using Cu Kα radiation was performed for phase identification.

The sliding wear properties of the laser-alloyed zone were evaluated with a ball-on-flat-type reciprocating wear tester using a 4.76-mm-diameter WC-Co ball as counterface material. The ball was ultrasonically cleaned with acetone and dried in air before it was mounted on the wear testing machine. The wear tests were performed without lubricants under the following conditions: temperature of 298 K, relative humidity of 50 %, sliding speed of 20 mm/s, amplitude of 5 mm, sliding distance of 72 m, and load of 0.98 N. The wear scars on the specimens and surfaces of the ball materials were investigated by SEM. A non-contact, three-dimensional measuring microscope was used to measure the depths of the wear scars.

3. Results and Discussions

Surface appearance and microstructure

Fig. 2 shows the appearance of the specimen after the laser alloying treatment. The surface of the titanium laser

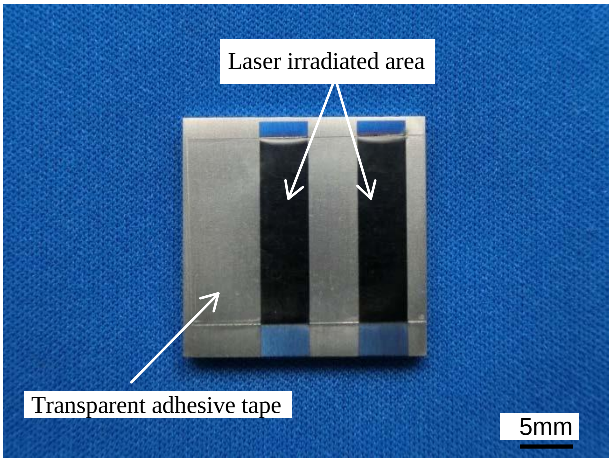

Fig.2 Appearance of the specimen after laser alloying.

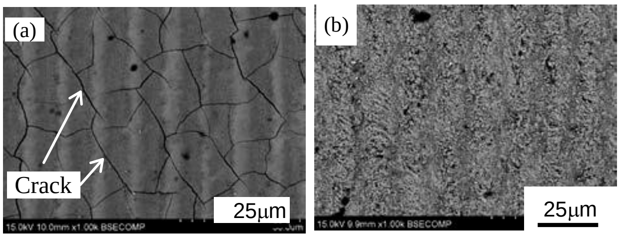

Fig.3 SEM images of the surface of the specimen.
(a) The area directly laser irradiated without the adhesive tape.
(b)The laser-alloyed zone with the adhesive tape.

irradiated through the adhesive tape was noticeably blackened. The surface irradiated without adhesive tape exhibited interference colors attributable to surface oxidation.

Under adequate laser conditions, the surface of the adhesive tape was not damaged due to the high laser transmittance of the adhesive tape. The thickness of the adhesive tape was thinner than the resin layer (0.2-mm-thick PMMA layer) we used in previous study [11]. However, the adhesive tape was not easily damaged by the nanosecond laser irradiation because the total heat input was lower than that of the CW laser.

The surface of the laser-alloyed zone was observed by scanning electron microscopy after removal of the adhesive tape and ultrasonic cleaning with acetone. Fig. 3 shows SEM images of the surface after laser irradiation. While no cracks were observed in the laser-alloyed zone (Fig. 3(b)), cracking was abundant in the area directly irradiated in air without the adhesive tape (Fig. 3(a)).

Fig. 4 (a) shows SEM images of the cross section of the specimen after laser alloying treatment. For comparison, Fig. 4 (b) shows the laser-alloyed zone formed by the CW laser in our previous study [11]. The thickness of the laser-alloyed zone formed by the nanosecond laser was about 5 - 10 μm, thinner than that of the CW laser. In the both laser-alloyed zone, the second phase particles formed by the reaction between the molten titanium and pyrolysis products of the resin, were observed. In the laser-alloyed zone formed by the nanosecond laser, the second phase particles were almost uniformly distributed, but in the case of the CW laser, the second phase particles were segregated in the top surface of the laser-alloyed zone. It seems that high peak power of the nanosecond laser promote the

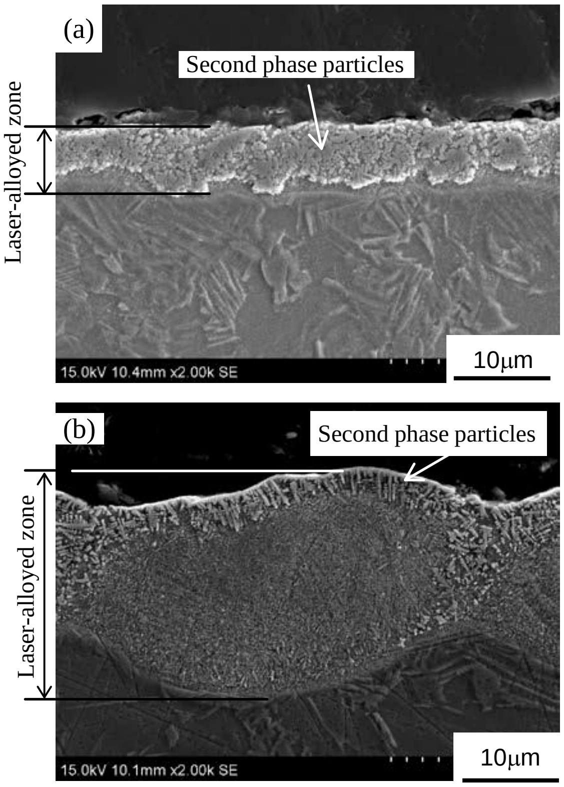

Fig.4 SEM images of the cross section of the specimen after laser alloying using (a) nanosecond laser (Average power 10W, Scanning speed 100mm/s, Scanning pitch 15μm) (b) CW laser (Power 30W, Scanning speed 150mm/s, Scanning pitch 50 μm).

stirring the molten pool, consequently the homogeneous concentration of alloying elements were achieved.

To compare the surface integrity of each laser-alloyed zone, surface profiles were measured by 3D measuring system attached to SEM (Hitachi, 3D-View) (Fig. 5). The surface roughness (arithmetic mean roughness Ra) of the laser-alloyed zone formed by the nanosecond laser was about 0.53 μm, while the value of the CW laser was about 2.36 μm. The surface roughness can be modified, if it is possible to reduce the scanning pitch. However, in the case of the CW laser, the resin layer was easily damaged due to large heat input, the laser-alloyed zone was not successfully obtained when the scanning pitch was reduced.

Phase identification of the laser-alloyed zone

Fig. 6 shows XRD results of the surfaces of the non-laser irradiated titanium substrate and the laser-alloyed zone. In addition to the peak of the α-titanium, a rock salt structure common to the TiC-TiN-TiO system was observed in the spectrum of the laser-alloyed zone.

The lattice parameter of this compound was calculated by using the diffraction peak corresponding to a (200) crystal plane, the diffraction angle 2θ was 40.23°. The calculated lattice parameter was 4.274Å, a value relatively close to the lattice parameter of TiN (4.242 Å). From the EPMA analysis, on the other hand, the nitrogen content of the laser-alloyed zone was found to be negligibly low. The adhesive tape contained no nitrogen as a composition element, and the surface of the tape prevented the entrainment of nitrogen from air.

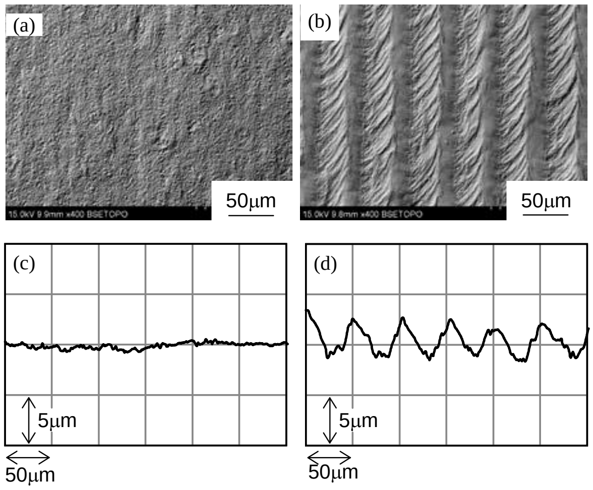

Fig.5 Surface topographic images ((a), (b)) and surface profiles ((c), (d)) of the laser-alloyed zone by SEM.
(a) ,(c) the laser-alloyed zone using nanosecond laser (Average power10W, Scanning speed 100mm/s, Scanning pitch 15μm)
(b),(d) the laser-alloyed zone using CW laser (Power 30W, Scanning speed 150mm/s, Scanning pitch 50 μm).

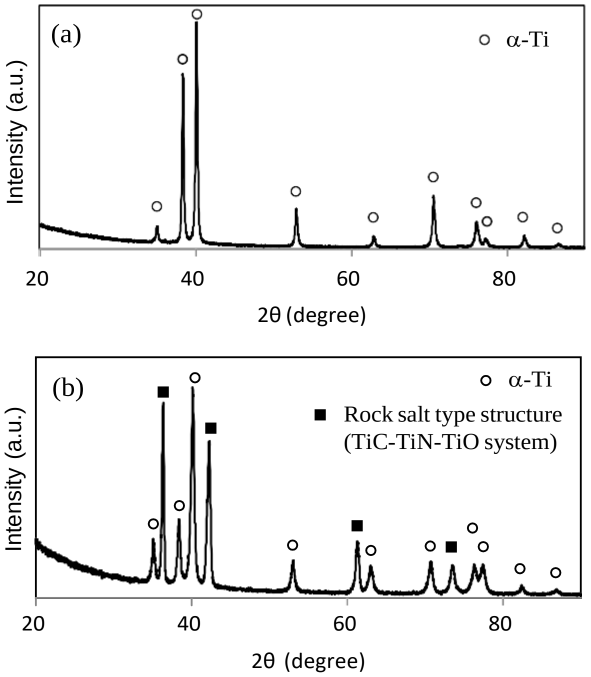

Fig.6 XRD patterns of (a) non-laser treated titanium substrate and (b) the laser-alloyed zone using nanosecond laser.

Fig. 7 shows the elementary distribution images by EPMA analysis. From these results, the second phase particles were found to be mainly composed of titanium and carbon. Slight amounts of oxygen were detected in the same area as the second phase particles. From these results, the second phase particles were identified as titanium oxycarbide. The XRD finding on the lattice parameter of the second phase particles, a value between TiC (4.327 Å) and TiO (4.177 Å), corresponded with this result. These

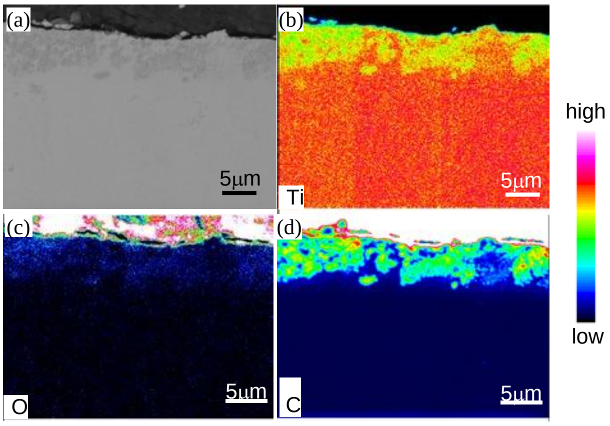

Fig.7 Results of EPMA plane analysis of the laser-alloyed zone using nanosecond laser.
(a) Secondary electron image (b) Titanium distribution image
(c) Oxygen distribution image (d) Carbon distribution image

carbon and oxygen elements were derived from the pyrolysis products of the acrylic adhesive. The laser irradiation induced the absorption of carbon and oxygen into the molten titanium, and the titanium oxycarbide formed during the subsequent solidification.

Wear properties

Fig. 8 shows the change of the friction coefficient at variable sliding distances. The friction coefficient of the non-laser treated titanium substrate ranged from about 0.5 to 0.8, while that of the laser-alloyed zone was markedly lower, at 0.2 to 0.3.

The adhesion and separation of the transferred particles induced sharp fluctuations in the friction coefficient of the non-laser-treated substrate to the WC-Co ball. The friction coefficient of the laser-alloyed zone, meanwhile, fluctuated much less than that of the titanium substrate.

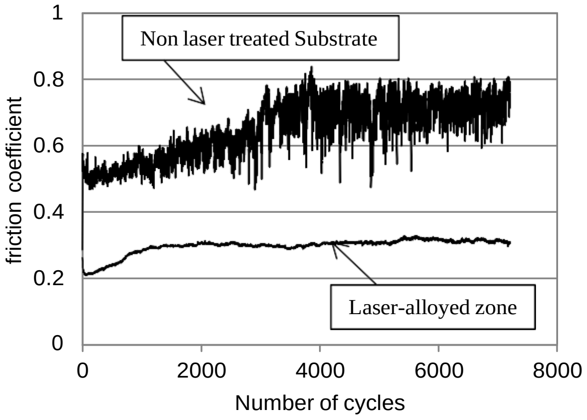

Fig.8 Friction coefficient during wear testing.

Fig. 9 shows SEM images of the specimen surfaces and the WC-Co ball counterfaces after wear testing. The wear scars on the non-laser-irradiated substrate were clearly observable and measured about 40 μm in depth in the assessment by the non-contact three-dimensional measuring microscope (Fig. 9 (a)). In contrast, the wear scars in the laser-alloyed zone were too shallow to clearly see (Fig. 9 (c)). The SEM image of the WC-Co ball after wear testing against the non-laser-treated substrate revealed many transferred particles derived from the adhesion of titanium (Fig. 9 (b)). Few transferred particles, meanwhile, appeared on the surface of the WC-Co ball after wear testing against the laser-alloyed zone (Fig. 9 (d)). EDS analysis revealed that these transferred particles were titanium oxides. It is known that low-tensile strength materials such as titanium exhibit great material transfer to nonmetallic counterfaces [12]. The great affinity of titanium for oxygen results in the formation of an oxide surface layer, which is transferred to and adheres to counter

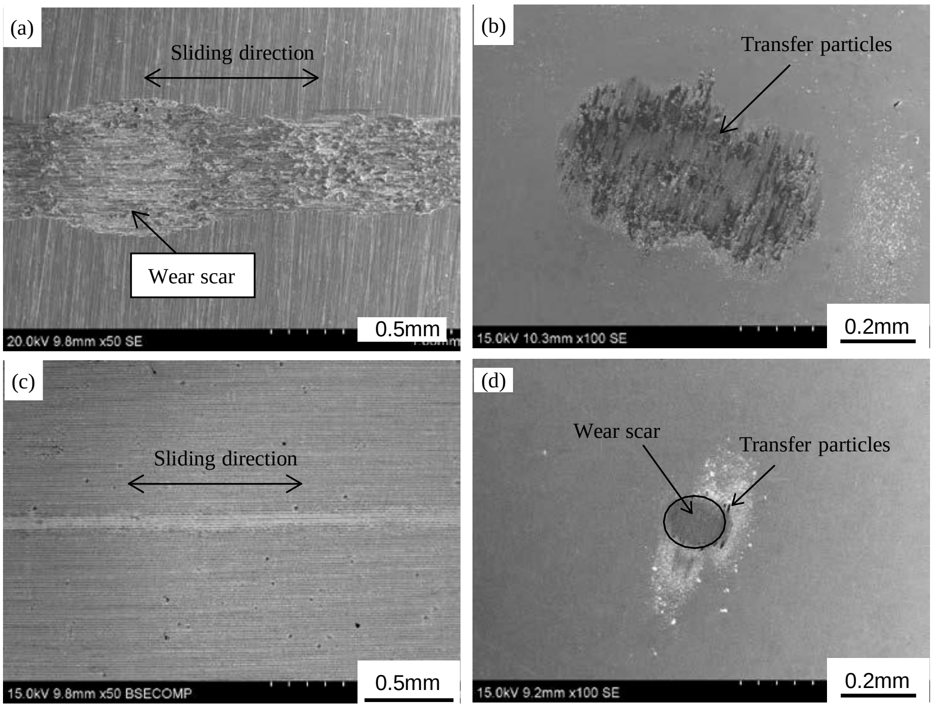

Fig.9 SEM images of the surface of the specimen ((a) non-laser treated substrate, (c) laser-alloyed zone) and the WC-Co ball after wear testing against non-laser treated substrate(b), and laser-alloyed zone(d).

materials. In the case of the laser-alloyed zone, the existence of titanium oxycarbide phase reduced the contact area of titanium and WC-Co, therefore adhesive wear was prevented.

The surface of the WC-Co ball was slightly worn after wear testing against the laser-alloyed zone (Fig.9 (d)). A. C. Fernandes reported that hardness of titanium oxycarbide decrease with increase oxygen content [13]. From the EPMA analysis, the X-ray intensity of oxygen was much lower than that of carbon (Fig.7), so the titanium oxycarbide obtained in this laser alloying process have higher hardness than WC-Co conterface material. As a result, the laser-alloyed zone was not abrasively worn by WC-Co. The laser-alloyed zone exhibited superior wear resistance.

4. Conclusions

Laser alloying of pure titanium using a nanosecond laser with a light-transmitting resin was carried out. A defect-free, laser-alloyed zone of about 5 - 10 µm in thickness was obtained. The laser-alloyed zone formed with the nanosecond laser was both shallower and smoother than the laser-alloyed zone formed by the CW laser. High volume fractions of titanium oxycarbide particles were dispersed in the laser-alloyed zone. The laser-alloyed zone had a low friction coefficient against the WC-Co ball and superior wear resistance.

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