JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 5 (1994) 692–694

The improvement of adhesion of polymer on titanium surface after treatment with TEA-CO_2 laser irradiation

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The application of a Mini-TEA-CO_2 laser for the modification of titanium surfaces to improve the bonding stability to a PMMA polymer is described. Cast and forged samples of titanium were treated with laser irradiation under different conditions. Depending on the kind of atmosphere employed during the laser treatment a differential change of bonding strength could be estimated. The compound stability was improved by a factor of 40 compared with the reference system. SEM pictures of the surface have shown that no cracks are formed but a modification of the laser-treated Ti surface topography similar to a freeze melting was observed. The results, found for a titanium dental polymer compound, should also be interesting for other medical applications.

1. Introduction

The reasons for medical and dental applications of titanium (Ti) or titanium alloys are the high toughness, the low specific weight, the corrosion stability, the high recovery rate of oxide layers (< 1 ms) and the biocompatibility. The high biological activity of Ti gives the possibility for its use in surgery (heart valves, endoprothesis, crowns, bridges implants [1–4]. For some applications it is necessary to combine Ti with other materials, such as polymers or ceramics. The interface of such compound systems is often the critical factor under applied loading conditions: thus the implant cement interface is described as unstable [5]. Also, the interface between Ti and a flame sprayed ceramic layer can be the weakest part of an implant [6]. The modification of the surface structure of these materials may result in enhanced interfacial bonding and improved biological performance. One surface modification technology under development is the TEA-CO_2 short laser pulse. This laser irradiation method results in improved surface properties. This study was made to determine if TEA-CO_2 laser treatment of Ti surfaces would result in improved metal–polymer bonding.

2. Materials and methods

The experiments are divided into the following parts:

(a) preparation of surface of Ti-samples, cleaning and smoothing;
(b) TEA-CO_2 laser treatment of Ti sample surfaces;
(c) preparation of Ti-PMMA compounds;
(d) testing of bonding stability under shear-stress loading conditions;
(e) scanning electron microscopic (SEM) investigations of laser-treated surfaces.

The metals used were pure castable Ti and Ti alloy. The bonding agent in the compound system was polymethylmethacrylate (PMMA) with a modified number of carboxyl groups, solved in acetacidethylesther (AAE). The main polymer of the compound system was a dental PMMA for the crown and bridge prostheses (Monopast). The preparation of the metal–polymer compound system was performed in the following way. Samples with dimensions of $10 \times 10 \times 5$ mm were cast or ground. The surface was smoothed with sandpaper of different size particles (220, 600, 800 SiC grit paper). Then the surfaces of the samples were treated by scanning with radiation from a Mini-TEA-CO_2 laser. The bonding agent was applied to the sample surfaces. Finally the surfaces were covered with 2 mm thick PMMA layers. Shear testing took place after immersion for 24 h in water at 37 °C. A universal testing machine was used to determine the shear stress at failure. All results were normalized to an area of 100 mm^2: i.e., the compound stability σ_v was calculated using the following equation: $\sigma_v = F/A$ (force/area) N/mm^2. Fig. 1 shows a schematic view of this test routine.

For all experiments a Mini-TEA-CO_2-Laser was used. The samples were treated at the focus of the laser radiation. The repetition rates were 3 Hz and 10 Hz.

ment. Additional improvement of compound stability after using a higher repetition rate was not observed, as shown in Fig. 3. The SEM micrographs, Fig. 4, show differences in the surface topography. SEM investigations showed that these treated Ti surfaces exhibited additional damage after stepping up the repetition rate: i.e. an increase in the numbers of cracks. Such cracks could reduce the stability of compound systems. For this reason, 3 Hz was used as the repetition rate in the following experiments.

The next step was to investigate the influence of the type of atmosphere streaming over the sample surface during the treatment with laser radiation. The influence of four different gases was tested; oxygen, nitrogen, helium and air. The results of bond strength testing are shown in Table I and Fig. 4. The bond

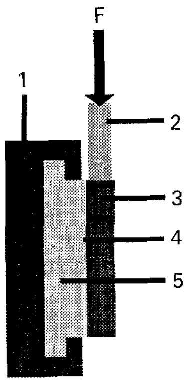

Figure 1 Schematic view of testing routine. (1 sample holder; 2 stamp of testing apparatus, 3 PMMA polymer; 4 bonding agent; 5 titanium sample).

The scan rate for the samples was 10 mm/min. The technical data for the laser and the data for this application are collected in Table I.

3. Results

Fig. 2 shows the results of compound stability for compound systems without and with laser treatment. It is seen that compound stability is improved by a factor of 40 compared to systems without laser treat-

TABLE I Laser parameters

Mini-TEA-CO_2-Laser parameters-specifications	
Pulse energy	180 mJ (multi mode) 120 mJ (TEM_{00} mode)
Peak power	2 MW
Pulse length	60 ns
Repetition rate	0–200 Hz
Gas mixture	$CO_2 + N_2 + He \cong$ 30 + 30 + 40 kPA
Wavelength	10.6 μm
Average power	max. 36 W
Efficiency	6–10%
Beam size	8 × 7 mm (multi mode) 5 mm (TEM_{00} mode)
Weight – laser head	10 kg
Dimensions – laser head (cylinder)	
length	35 cm
diameter	20 cm
Lens	Zn-Se-lens (f = 180 mm)

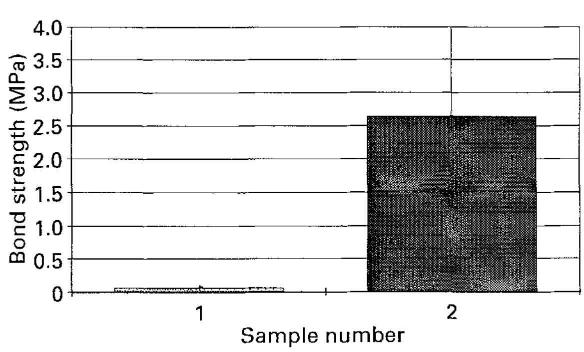

Figure 2 Compound stability for compound systems without (1) and with (2) laser treatment.

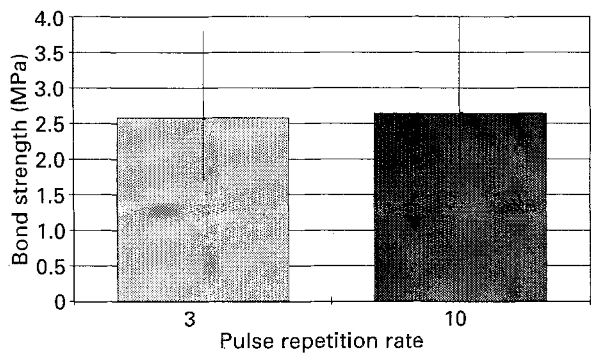

Figure 3 The influence of the pulse repetition rate on the bonding stability of laser-treated Ti–PMMA compound.

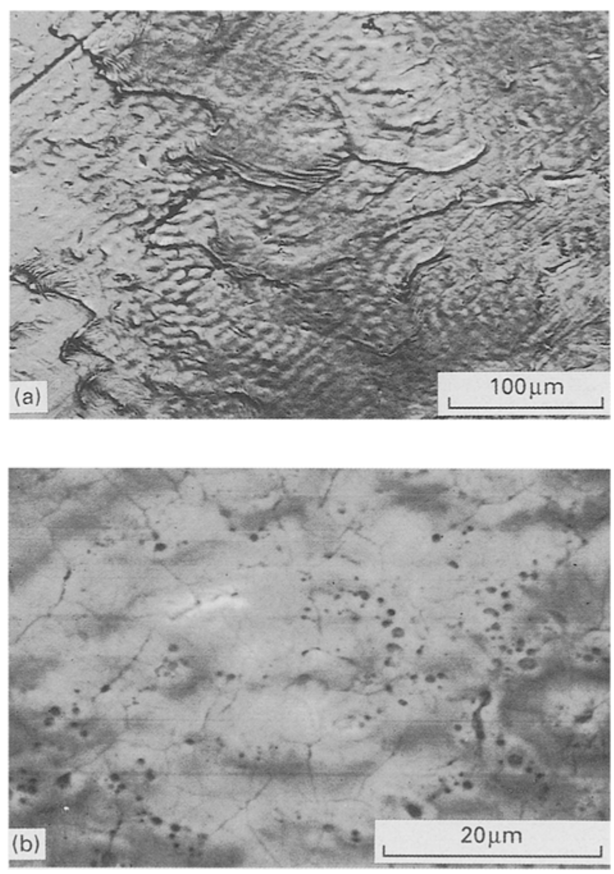

Figure 4 SEM micrographs of laser-treated Ti surfaces under oxygen atmosphere: (a) repetition rate 3 Hz, frozen melting; (b) repetition rate 10 Hz, cracks.

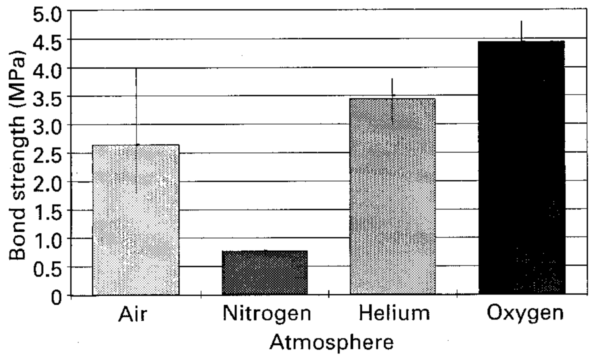

Figure 5 The influence of the type of atmosphere on the bonding stability of laser treated Ti–PMMA compound.

strength was between 13 and 74 times higher than the reference samples. The nitrogen atmosphere had a significant influence, resulting in the lowest values of estimated bond strength. The atmosphere of most interest is oxygen. So the most stable compound systems could prepare and moreover the surface topography was completely different. The SEM pictures (Fig. 4) have shown a structure similar to a frozen melting.

4. Discussion

The result of TEA-CO_2 laser treatment of a Ti surface is a physico-chemical modification. The reason is the ablation of the adsorbed layer and the creation of a plasma plume near the sample surface. The plasma plume is created by the use of very small period pulses and high laser power, giving a pulsed power in the range of megawatts. The focusing of the radiation produces intensities of more than $100\ MW/cm^2$. Under these conditions the treated sample shows non-linear behaviour (photo ablation, breakdown, photo disruption). The high intensity of the laser radiation produces a high electric field strength and so a breakdown at the surface, as with an electrical spark. Therefore the absorption properties of the material do not play an essential role [8–12]. This is the reason for a transfer of energy independent of the wavelength of the radiation and the dissipation of energy in the surface layer of the sample. In this way meta-stable states can be produced at the surface. These meta-stable states can improve the wettability for the bonding agent and the bonding strength. The number and the nature of such meta-stable states is dependent on the type of reaction atmosphere. Thus different colours, gold-yellow under nitrogen, dark blue under oxygen, are observed. These changes of the colours and the differences in the topography, only cracks under nitrogen and frozen melting under oxygen, onto the Ti surfaces give the reason for the interpretation of improvement of bonding strength with help of creation of meta-stable, non-stoichiometric Ti oxides onto the surfaces. These meta-stable non–stoichiometric Ti oxides should be able to create chemical bonds to the polymer, like the modified PMMA.

The results, obtained for a titanium dental polymer compound, should also be interesting for other medical applications.

Acknowledgements

This study was supported by the BMFT grant 13 N 5911, BEGO Cop. Germany, LINK Cop. Germany and VITA Cop. Germany. We have to thank Mrs Chr. Schoepf for her technical assistance.

References

1. A. R. HRUSKA, *Die Quintessenz* **1** (1988) 35.
2. A. CIGADA, M. CABRINI and P. PEDEFERRI, *J. Mater. Sci.* **3** (1992) 408.
3. D. F. WILLIAMS, in "Biocompatibility of clinical implant materials" Vol. I, edited by D. F. Williams (CRC Press, Boca Raton FL, 1981) p. 9.
4. P. B. BANNON and E. F. MILD, in "Titanium alloys in surgical implants ASTM STP 796", edited by H. A. Luckey and F. Kubli Jr (Philadelphia, 1983) p. 7.
5. J. A. JOHNSON, J. W. PROVAN, J. J. KRYGIER, K. H. CHAN and J. MILLER, *J. Biomed. Mater. Res.* **23** (1989) 819.
6. CH. MÜLLER-MAI, H.-J. SCHMITZ, V. STRUNZ, G. FUHRMANN, TH. FRITZ and U. M. GROSS, *ibid.* **23** (1989) 1149.
7. E. REICHEL, and SCHMIDT-KLOIBE in "Angewandte Lasermedizin" edited by Laser-Medizinzentrum-Berlin (Berlin 1990).
8. J. WINNACKER. in "Physik von Maser und Laser" (Bibliographisches Institut, Wissenschafts-verlag, Mannheim, Zurich, 1984).
9. F. K. KNEUBUHL and M. W. SIGRIST, in "Laser" (Teubner-verlag Studienbücher Physik, Stuttgart, 1988) p. 65.
10. W. BRUNNER and K. JUNGE in "Lasertechnik: Eine Einführung" edited by Dr Alfred Hüthig (Verlag, Heidelberg, 1987).
11. J. WEBER and W. HERZIGER in "Laser-Grundlagen und Anwendungen" (Weinheim: Physik Verlag, 1972).
12. J. WILSON and J. F. B. HAWKES in "Optoelectronics: an introduction" (Prentice-Hall, London, 1983).