JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **8** (1997) 781–784

Characterization of microblasted and reactive ion etched surfaces on the commercially pure metals niobium, tantalum and titanium

C. M. J. M. PYPEN*, H. PLENK Jr
*Department of Bone and Biomaterials Research, Histological-Embryological Institute, University of Vienna, Schwarzspanierstraße 17, 1090 Vienna, *and also Department of Oral Surgery, Dental University Clinic, University of Vienna, Währingerstraße 25a, 1090 Vienna, Austria*

M. F. EBEL, R. SVAGERA, J. WERNISCH
Institute of Applied and Technical Physics, Technical University Vienna, Wiedner Hauptstraße 8-10, 1040 Vienna, Austria

In surface-roughened metallic implant materials, the topography, chemistry and energy of the surfaces play an important role for the cell and tissue attachment. The highly reactive commercially pure metals niobium, tantalum and titanium were analysed after microblasting (with Al_2O_3 powder and consecutive shot-peening with $ZrSiO_2$), and after additional reactive ion etching (RIE, with CF_4). Scanning electron microscopy in combination with energy-dispersive X-ray analysis and surface roughness measurements showed, for all microblasted surfaces, a heterogeneous roughening (R_a about 0.7 μm), and a contamination with blasting particles. RIE resulted in a further roughening (R_a about 1.1 μm), and a total cleaning from contaminations, except for traces of aluminium. Determination of surface energy by dynamic contact angle measurements showed an increase in surface energy after microblasting, which further increased after RIE, most pronounced for commercially pure niobium. In conjunction with superior electrochemical properties, this makes niobium and tantalum promising candidates for implant purposes, at least equal to the generally used titanium.

1. Introduction

It is well known that the surface topography, surface energy and surface chemistry govern the biological response to an implant. Various blasting techniques are used to produce irregularly roughened metallic implant surfaces, resulting in high percentages of osteoblast cell attachment *in vitro* [1], and in better bone apposition and fixation *in vivo* [2, 3]. Contaminant films, resulting from these preparative procedures, affect the surface composition and energy, and induce adverse cellular responses [4–6]. Radiofrequency glow-discharge treatment with argon or air was found to be an effective method for removing these films and cleaning the surfaces. In addition, the resulting high-energy surface state enhances cellular adhesion [7]. A main drawback to these commonly used plasma cleaning methods is the contamination of the cleaned surface with impurities that are desorbed from the glass wall of the process chamber [5, 8].

The chemical properties of the implant surface and thus the interface chemistry, influencing close bone apposition to the implant, are determined by the oxide layer and not by the metal itself [5]. The highly reactive commercially pure metals niobium and tantalum offer even more stable oxide layers [9] than the commercially pure titanium, and equal mechanical properties have been shown by our group [10, 11], but not much is known about the respective surface properties.

The purpose of the present work was to introduce new surface preparation techniques, and to characterize the resulting surface properties on these metals which are expected to improve biomaterial–bone tissue interactions.

2. Materials and methods

2.1. Materials

Discs (diameter 13 mm × 2.5 mm) were cut from rods of the commercially pure metals niobium (cp. Nb). tantalum (cp. Ta) and titanium (cp. Ti). All discs were wet ground until no. 4000 grit SiC, ultrasonically (US) cleaned for 20 min in 96% ethanol and dried.

A first group of the samples was examined as-ground and US cleaned; a second group was microblasted

Selected paper from the 13th European Conference on Biomaterials, Göteborg, Sweden.

at 0.5 bar with Al_2O_3 (grain size 30–40 μm), consecutively shot-peened at 3 bar with $ZrSiO_2$ powder (grain size 20–30 μm) and US cleaned. A third group of samples was microblasted, shot-peened and then reactive ion etched (RIE). The RIE was done in a custom-made apparatus, designed and manufactured at the Technical University Vienna. The samples were placed in an anodized aluminium chamber, which was evacuated to 1 mbar, and were etched for 5 min in a radio-frequency initiated CF_4–oxygen plasma (95/5 mixture) at a frequency of 100 kHz, with an effect of 100 W. These samples were consecutively etched for 30 s with pure oxygen under the same conditions and finally US cleaned. All samples were stored in a desiccator before examination.

2.2. Surface characterization

The effect of the different surface treatments on the surface topography was characterized by scanning electron microscopy (SEM) on a Jeol 330A. Eventual surface contaminations, due to the grinding and/or blasting, were analysed by energy dispersive X-ray analysis (EDX).

The influence of the surface structuring and the consecutive cleaning on the composition of the surface oxide layer was determined by X-ray photoelectron spectroscopy (XPS) on a Kratos XSAM 800, using MgK_α radiation.

Eventual changes in surface energy, due to the surface treatment, were measured in a contact angle measuring system (G1/G4, Krüss Comp., Germany). A series of isopropanol–water mixtures (0%–100%, 5%–95%, 10%–90%, 15%–85%) was used and for each fluid 100 measurements of the dynamic contact angle were made. The surface energy was calculated using the method of Owens–Wendt–Rabel.

Surface roughness was measured on a Rodenstock RM100. For each surface a total of 20 roughness measurements was done on three samples, and the roughness for this surface expressed as mean R_a value.

3. Results and discussion

3.1. Topography

For all metals, SEM of the ground surfaces revealed a uniformly smooth surface with preparation scratches, on which no morphological contamination was detected (Figs 1a and 2a). After microblasting and shot-peening the surfaces appeared heterogeneously roughened (Figs 1b and 2b). Contaminations, embedded during the blasting, were seen on the surface. RIE resulted in an additional roughening of the surfaces with an superimposed submicrometre etching (Figs 1c and 2c). Morphological contamination was no longer visible on the etched surfaces.

Roughness values, R_a, revealed a significantly increased surface roughness after blasting and an even more pronounced additional roughening after RIE (Fig. 3). The measured values confirmed the SEM impression (Figs 1c and 2c).

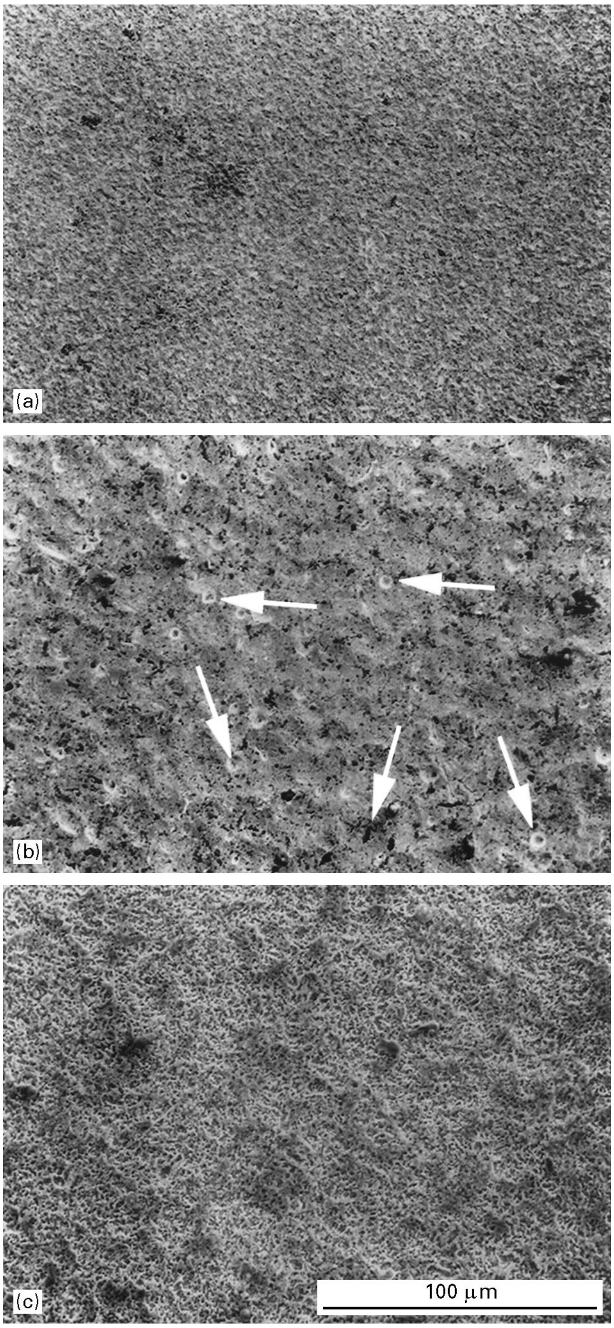

Figure 1 Topography of cp. Nb after (a) grinding, (b) blasting, and (c) blasting followed by RIE. Contaminations are marked by arrows.

3.2. Contaminations

EDX spectra of the ground surfaces showed minor Si contaminations, resulting from the SiC grinding. After microblasting, a major Al and Zr contamination was detectable, as well as a minor Si contamination, all resulting from the blasting powders. This confirmed the findings from Ricci *et al.* [6], who measured Al and Si contaminations on blasted surfaces. After RIE, the Zr and Si contaminations were totally removed, and the amount of Al contamination drastically reduced.

Analyses with XPS of the metal oxide confirmed the presence of the same contaminations on the microblasted surfaces (Fig. 4). A total removal of the Zr and Si contamination was confirmed, as well as the reduction of the Al contamination. A full removal of the

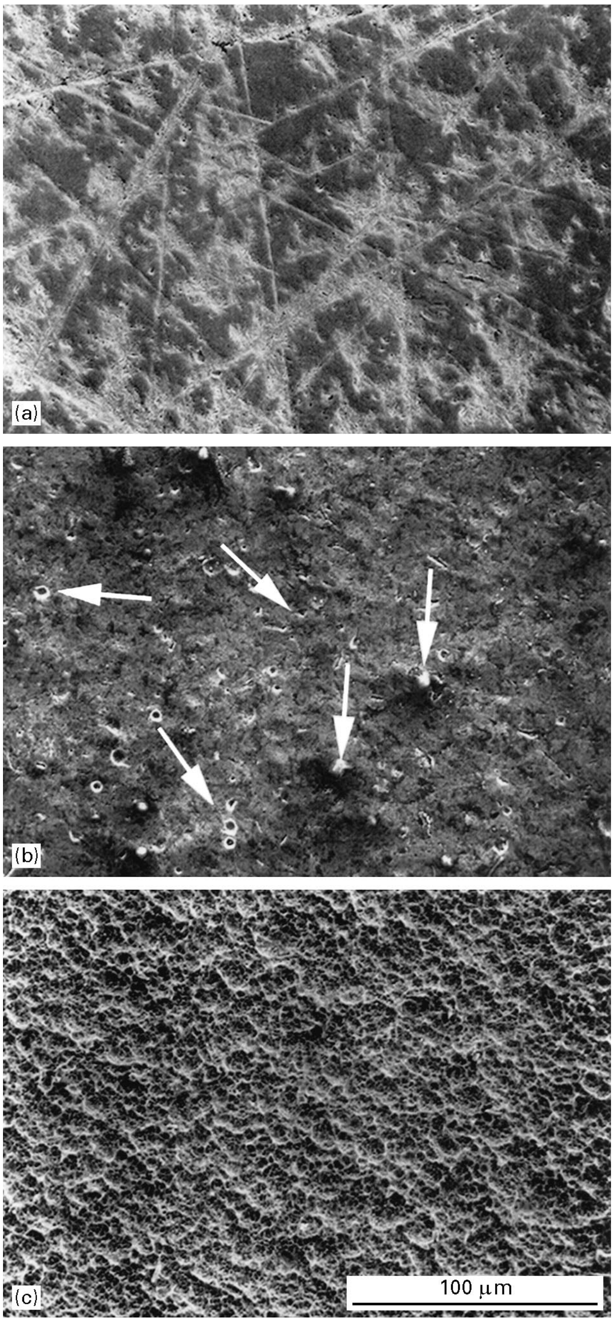

Figure 2 Topography of cp. Ti. (a)–(c) See Fig. 1.

Al_2O_3 blasting particles, deeply embedded into the metal due to their hardness and sharp edges, would apparently require longer etching of the surrounding metal oxide. No Si or Na contamination, resulting from the etching chamber, was found, as was the case for the conventional plasma etching with argon or air [5, 8].

Furthermore, XPS analyses revealed that, after RIE, the surface was contaminated with F (from the etching plasma). It has been shown that this F can totally be removed by heating up the sample, as e.g. up to 300 °C for 2 h for cp. Ta [12] which should not affect the mechanical properties.

From the XPS spectra it was seen that after RIE with oxygen plasma, the thickness of the oxide layer was increased, e.g. from approx. 3 nm to more than 10 nm for the cp. Ta.

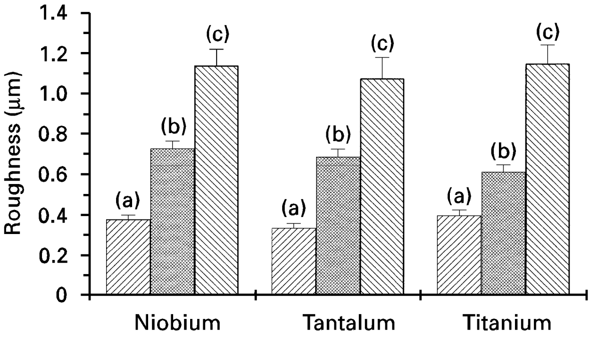

Figure 3 Mean roughness values, R_a, for cp. Nb, cp. Ta and cp. Ti after (a) grinding, (b) blasting, and (c) blasting followed by RIE.

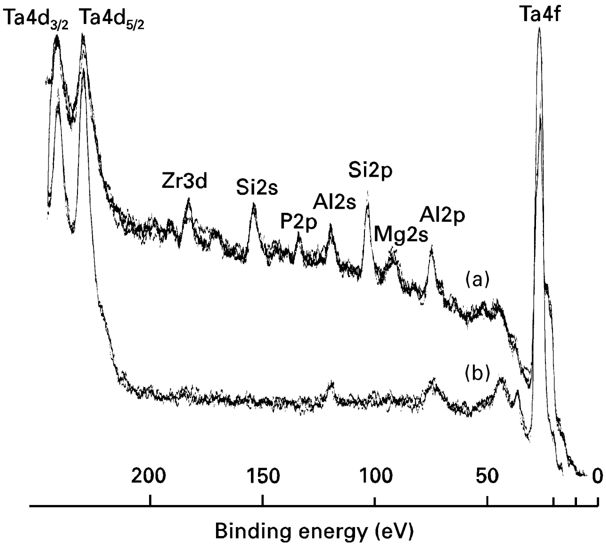

Figure 4 XPS spectrum for microblasted cp. Ta (a) before and (b) after RIE.

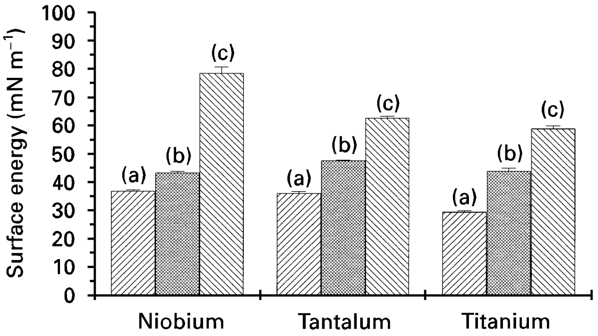

Figure 5 Surface energy for cp. Nb, cp. Ta and cp. Ti after (a) grinding, (b) blasting, and (c) blasting followed by RIE.

3.3. Surface energy

For all cp. metals, the surface energy was significantly increased after blasting. RIE resulted in a significantly higher surface energy compared with the ground and microblasted surfaces (Fig. 5). This effect was most pronounced for cp. Nb. Higher surface energy correlates with increased wettability which was found to induce an improved cellular attachment [13].

4. Conclusion

Blasting followed by reactive ion etching resulted in homogeneously roughened, contaminant-free and high-energy surfaces on all metals which may improve cell and bone tissue attachment.

RIE with a CF_4–oxygen plasma may be preferable to conventional plasma etching, because no Si and/or Na contamination from the plasma and/or from the etching chamber is deposited on the sample surface. Because Si can be totally removed after RIE, a conventionally sand-blasted surface will be fully contaminant-free after RIE.

However, great attention must be paid to the removal of Al in the oxide layer which might impair bone mineralization.

Acknowledgements

This study was supported by the Fonds zur Förderung der Wissenschaftlichen Forschung in Austria, project no. P-09295-MED, and the Biomed-2 project no. BMH4-CT96-1135.

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Received 5 May
and accepted 15 July 1997