Acid Etched Porocoat® of CoCrMo for Biological Fixation

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Statement of purpose: Since the initial application of plasma sprayed hydroxyapatite (PSHA) coatings on dental implants two decades ago, topographic modification of dental implants has been the subject of numerous investigations. The use of acid etching methodologies produces permanent surface modifications of metal surfaces, which typically consist of micron and submicron surface voids. The use of acid etching to modify the surfaces of Ti6Al4V (Ti64) implant materials has been shown to be an effective method to accelerate bone apposition and implant fixation [1]. Acid etched Ti64 surfaces have advantages over PSHA coatings such as free of coating delamination, 3rd body wear particles generation, fewer restrictions on sterilization, and increased shelf-life. However, while acid etching has become the gold standard method of surface texturing for dental implant fixation, this popularity has not transferred into orthopaedics. Porous coating (sintered metal beads or plasma sprayed metal substrate) has been largely used in orthopaedic to improve implant mechanical fixation to bone. In knee arthroplasty, CoCrMo is used exclusively for the femoral component due to its low wear and corrosion resistance. Fixation of CoCrMo porous coating is not as ideal as Ti64. Biological fixation improvement can be achieved by surface modifications. One such attempt is to use acid etching (AE) to generate osteophilic surface. Prior animal study showed that AE-Porocoat® (PC) of CoCrMo significantly improved biological fixation in a canine lateral condyle gap model [2].

The aim of this investigation is to characterize the effect of AE on surface chemistry and topographical changes of CoCrMo PC. AE on PC adhesion and fatigue limit of the substrate were also tested.

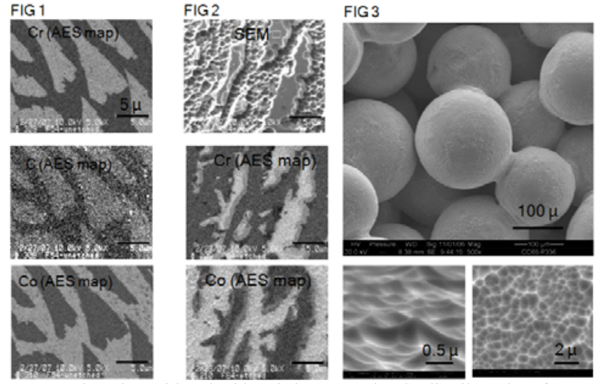
Methods: CoCrMo PC was sintered on 1 inch diameter and 0.125 inch cast CoCrMo disc (ASTM F75) substrates in a vacuum furnace. Sintered PC was acid etched with a mix of hydrochloric acid and ammonium persulfate at room temperature. The etched parts were then ultrasonically cleaned in RO water and dried at 60 °C in an oven prior to further testing. Auger Electron Spectroscopy AES and X-ray Photoelectron Spectroscopy (XPS) were employed to characterize the resultant surface chemistry (Co, Cr, Mo, C, O) of the etched PC beads. Secondary electron images (3KeV) at zero and +/- 5° tilting angles were collected followed by 3-D image reconstruction using MeX Professional v5.0 (Alicona, Germany). Surface profile parameters (Table 1) were evaluated with Mex software.

After hot isostatic press and homogenization, twenty-four (24) cast CoCrMo bars (0.5 inch diameter and 9.5 inch long) were sintered with 3 inch CoCrMo PC. Twelve (12) acid-etched and twelve (12) as-sintered PC bars were subjected to four point bending fatigue testing. The load span was 2 inches and the support span was 6 inches. Samples were loaded at various stress levels (40-80ksi, 10Hz) to determine fatigue limit at 10 million cycles. For static pull-out, twenty (20) shear pins (1/8 inch diameter and 5 inch long) were prepared with one end porous coated. Ten of the shear pins were acid etched. The PC regions of shear pins were fully immersed in a liquid resin and cured at room temperature overnight. Bonding integrity of AE-PC was evaluated by failure load and failure mode.

Results: AES mapping of sintered PC shows that the surface of a CoCrMo bead consists of a Cr carbide-free and Cr carbide-rich regions, where Cr carbides are several microns wide and tens of microns long (Fig. 1). The Cr carbide is roughly 30-40 nm thick as shown by the depth profile analysis (data not shown). The Cr carbide-free area is covered with a thin layer of Cr oxide (<5 nm). Bead surface carbide distribution may vary with bead sintering as well as the carbon content of substrate. After acid etch, micron and submicron textures developed on the carbide-free area with residual carbides on the surface (Fig. 2). Compared to the smooth appearance of the as-sintered bead, the acid etched bead shows randomly distributed surface voids ranging from 0.2μ to about 5 μ (mode=0.7 μ) in lateral dimension and a depth ranging from several tens of nanometers to half a micron (Fig.3).

3-D images of a region of the as-sintered and acid etched CoCrMo bead

FIG 1 FIG 2 FIG 3



were analyzed. Acid etched bead shows randomly distributed surface voids of irregular shapes while the as-sintered bead has relatively smooth appearance with concentric steps due to thermal etching during the sintering process. Table 1 summarizes the analyzed topographic parameters. There are no significant changes of the conventional roughness parameters (Sa, Sq, Sz) with acid etching. Instead, most significant changes due to acid etching were observed in peak density (# of peaks/μ^2) and peak spacing. There are about thirty to forty-fold increase of peak density and about seven fold reduction of peak spacing for the acid etched bead in contrast to the as-sintered one. The acid etching process produces permanent micro texturing modifications on

Table 1 Surface roughness, amplitude distribution and peak spacing*

Parameter	Sa (nm)	Sq (nm)	Sz (nm)	Ssk	Sku	peaks/μ^2	mean±std (μ)*
acid etch	178	237	4.51	-1.47	0.91	1.51	0.90±0.46
as-r	231	347	4.88	-1.26	1.02	0.04	6.26±3.56

the CoCrMo PC bead surface. The surface topographical features after acid etching were sub-cellular in size, which may help retain serum proteins and strengthen the fibrin attachment during wound healing process [3]. The 4-point bending fatigue testing showed the fatigue limit (10 million) of AE-Porocoat® sample was 45 ksi, which was no less than that of the as-sintered PC (40 ksi). There was no delamination of as-sintered or AE-Porocoat® in any of the tested fatigue samples. In the resin pull-out test, AE-Porocoat® exhibited higher pull-out strength (38.3 ± 1.2 MPa) than as-sintered Porocoat® (33.0 ± 3.5 MPa). Neither as-sintered PC nor AE-PC showed coating delamination or loose beads in resin. Combining the surface texture produced by the acid etching process with a rough macro porous structure could provide both the mechanical and biological means to enhance implant fixation that would benefit uncemented knee replacement

Conclusions: Submicron indentations were produced on CoCrMo surface by acid etching. Acid etch dramatically increased the feature (indentation) density. The acid etch process did not affect the mechanical integrity of PC or fatigue of the treated substrate.

References:

[1] Hackings et al. JBJS (Br), 2003; 85-B: 1182-9
[2] Stahlschmidt et al. Poster# 2068, 56th ORS
[3] John Davies. Journal of Dental Education, vol. 67(8), 2003: 932:949