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CoCr F75 scaffolds produced by additive manufacturing: influence of chemical etching on powder removal and mechanical performance

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ABSTRACT

Additive manufacturing techniques such as Selective Laser Melting (SLM) allow carefully controlled production of complex porous structures such as scaffolds. These advanced structures can offer many interesting advantages over conventionally produced products in terms of biological response and patient specific design. The surface finish of AM parts is often poor because of the layer wise nature of the process and adhering particles. Loosening of these particles after implantation should be avoided, as this could put the patient's health at risk. In this study the use of hydrochloric acid and hydrogen peroxide mixtures for surface treatment of cobalt-chromium F75 scaffolds produced by SLM is investigated. A 27% HCl and 8% H₂O₂ etchant proved effective in removing adhering particles while retaining the quasi-static and fatigue performance of the scaffolds

KEYWORDS

Selective laser melting (SLM); CoCr scaffolds; surface roughness; surface modification; biomaterials; additive manufacturing

1. INTRODUCTION

A porous structure is characterized by its parent material and by the unit cell characteristics such as type, size, and relative density. When a biocompatible material such as CoCr is used to produce these porous structures, they can be considered porous metallic biomaterials. By changing the unit cell characteristics, unique properties and thus improved orthopedic implants can be obtained (Gibson and Ashby 1988). Two of the reasons porosity is added to these implants are (i) an enhancement of the osseointegration and (ii) a reduction of the stress shielding effect (Karageorgio and Kaplan 2005, Alvarez and Nakajima 2009). The seamless integration of porous structures in larger, complex constructions and the unique geometries possible when using additive manufacturing (AM) techniques can extend these applications further.

Several authors have studied the potential of CoCr implant production by AM already. Kircher et al. were the first to report the production and characterization of dense CoCr structures by Electron Beam Melting (EBM) (Kircher et al. 2009). The fatigue of non-porous CoCr samples produced by SLM was studied by Haan et al. in (Haan et al. 2015). They found that the AB material did not perform as well as cast CoCr because of residual stresses and remaining porosity. After a Hot Isostatic Pressing heat treatment, the material produced by SLM showed better fatigue performance than the as-cast material. This result shows the potential of SLM-produced CoCr for fatigue applications if the production process and microstructure are well controlled. Hazlehurst et al. have experimentally and numerically investigated the potential of SLM-produced functionally graded CoCr femoral stems to reduce stress shielding (Hazlehurst et al., 2014a, b, 2013a,b). They obtained a 60% less stiff implant by the incorporation of porous zones in the implant but stress that a thorough fatigue test would be necessary before their design can be used in vivo. Limmahakun et al. have recently studied the quasi-static mechanical properties of porous CoCr structures produced by SLM (Limmahakun et al. 2017). They agree with Hazlehurst et al. that this technology has great potential for reduction of stress shielding in femoral stems.

While AM can be used to build porous structures with a controlled geometry, it offers limited control of surface quality. The as built (AB) surface quality of products manufactured by AM is often poor, as powder particles are partially melted onto the surface. This has important implications for medical applications due to the influence of surface quality on both fatigue resistance and cytocompatibility (Kotousov et al. 2011). In addition, AM-produced metal implants can cause metallosis when partially bonded are released. In order to improve the surface quality of AM products, chemical etchants to reduce surface roughness can be used (Pyka et al. 2012). These etchants must be tailored to a particular material as well as a particular scaffold (Pyka et al. 2013). Most of the research in this field has focused on the well-known titanium alloys, such as grades 5 and 23. Just like Ti alloys, CoCr alloys are widely used in medical applications, especially in orthopedic and dental implants (Sykaras et al. 2000). However, there has been no study on the improvement of the surface quality of AM-produced CoCr implants so far. The development of such a treatment could be even more important than for Ti alloys, as cobaltism is an established health concern (Sansone et al. 2013). Therefore, the aim of this research is (i) to develop a chemical

etching treatment to improve the surface quality of SLM-produced CoCr F75 scaffolds and (ii) to study the influence of this treatment on the fatigue properties of these scaffolds.

The results show that an etchant based on HCl and H₂O₂ can be successfully used to remove the residual powder particles. The surface was investigated using different image based roughness measurements. SEM micrographs, metallographic cross-sections and cross-sections reconstructed from X-ray computer tomography (X μ CT) images were used. In addition, quasi-static and dynamic compression testing was used to investigate the influence of the chemical etching treatment on the mechanical behavior. It was found that the developed surface treatment did not improve nor degrade the fatigue life of the scaffolds tested.

2. MATERIALS AND METHODS

Five different groups of CoCr scaffolds were produced using Selective Laser Melting (SLM) as indicated in Table 1. Magics software (Materialise NV, Belgium) and DMP (direct metal printing) control software (3D Systems Leuven, Belgium) were used for build file preparation. A diamond unit cell was chosen for two reasons: (i) its struts are oriented beneficially for the SLM process and (ii) this structure behaves isotropically under mechanical load (Yasa and Kruth 2011, Ahmadi et al. 2014). The size of the unit cell a was 1.5 mm for all the samples. The samples have a cylindrical geometry with height H and diameter d as indicated in Figure 1 and Table 1. As starting material an ASTM F75 grade gas atomized powder was used. The scaffolds were produced using a ProX DMP 320 machine. Both the machine and powder were supplied by 3D Systems. The longitudinal axis of the samples was oriented perpendicular to the building plate.

Scaffold groups A, C and E were analyzed in the as-built condition, while scaffold groups B and D were chemically etched after SLM before further analysis. In order to facilitate comparison scaffold groups B and D were designed and printed with thicker struts as to match the relative density of scaffold groups A and C after the etching step. The relative density in this work is defined as a property of the porous sample and relates the volume of solid material to the total volume of the sample. Scaffold group E has a higher actual relative density to study the effect of relative density on the mechanical performance. Table 1 also shows the difference between the designed relative density and the actual relative density which is measured in the as-built condition for samples A, C and E and after etching for groups B and D. Due to specific SLM process conditions, the actual relative density in the as-built condition is always higher than the designed relative density. This can be compensated for by post treatment steps, such as etching.

Table 1 Properties of the five different scaffold groups (A-E) used in this research

	A As-built	B Etched	C As-built	D Etched	E As-built
Scaffold diameter D (mm)	6	6	15	15	15
Scaffold length L (mm)	8	8	20	20	20
Designed strut diameter d (μm)	200	230	200	230	230
Unit cell size a (mm)	1.5	1.5	1.5	1.5	1.5
Designed Rel. density (%) of samples	25	32	25	32	32
Actual Rel. density (%) of samples	28.5	28.7	28.6	29.5	36.1
Rel. density of material (%)	98.3 $\pm$ 0.8	97.8 $\pm$ 0.9	98.7 $\pm$ 0.15	98.2 $\pm$ 0.20	98.4 $\pm$ 0.17

The relative density of the solid structure itself was measured using the Archimedes method in alcohol. The results summarized in Table 1 show that this value is consistent for all samples. With material densities of around 98% some porosity inside the struts can be expected. The samples were subsequently further analyzed by X-ray Computer Tomography. The X μ CT scans were performed with the Phoenix NanoTom S using a tube voltage of 120 kV, a current of 115 μA , a 0.1 mm copper filter, 500 ms exposure and a resolution of 4.25 μm per voxel. A 3D model was generated for the scaffolds in the different as processed conditions using the X μ CT data. These 3D reconstructions were then analyzed using the CTAn software package (Bruker MicroCT, Kontich, Belgium). By fitting spheres inside the solid structure in the model a distribution of the strut thickness was obtained. Figure 2 shows the cumulative strut thickness distribution of as-built scaffolds and the etched scaffolds. The strong similarity of the two sets indicates that the steps taken during build file preparation to compensate for the material loss during etching were successful and also validates the comparisons of their mechanical properties. All surface roughness tests were performed on the smaller scaffolds (A, B) and mechanical testing was performed on larger samples (C, D and E) to eliminate the size effect reported in (Andrews et al. 2001, Onck et al. 2001).

Surface roughness was measured using longitudinal cross sections of scaffolds. These were created using both the X μ CT 3D reconstructions (see Figure 2 B) or from physical cross-sections as obtained by metallography (see Figure 4). For metallography scaffolds were embedded in liquid resin (KEM90, ATM GmbH, Germany) followed by infiltration under vacuum. Samples were ground and polished according to standard metallographic practice and images were made with a Nikon Eclipse MA 100 microscope (Vander Voort 1984). Electrochemical etching in 10 % HCl (7V, 6s, graphite counter electrode) was used to visualize the microstructure and melt pools of the metallographic samples.

In order to ensure worst case conditions all roughness measurements were performed on the bottom side of the struts. Due to the SLM process this side has the highest fraction of attached particles and can be assumed to have the highest roughness. It is also the side which should benefit most from particle removal by etching. The roughness measurements themselves were performed in MATLAB using the methodology outlined by Kerckhofs et al. (Kerckhofs et al. 2012) and based on the deviation from the mean surface (see Figure 5).

For each roughness measurement, using X μ CT produced images, an image slice was chosen from the approximate middle of the stack (central plane of the scaffold). These images showed the largest fraction of metal and the largest apparent strut thickness. The roughness of four strut surfaces was measured. A second and third image slice were chosen at a distance of approximately 15 slices (approximately 64 μ m) from the first, central image and the measurements were repeated. In total 12 measurements were performed per surface treatment.

Fatigue tests were performed on an Instron Electropuls E10.000 with 10kN force cell at room temperature (20 $\pm$ 2°C) and at relative humidity of 50 $\pm$ 5%. All fatigue samples were subjected to constant amplitude sinusoidal loading in compression-compression at fixed test frequency of $f=15$ Hz and fixed load ratio $R=0.1$. All experiments were force controlled and hence the stress based (SN) approach was used for fatigue analysis. Three sample conditions were studied:

- As-Built (AB) with relative density 36.1% $\pm$ 0.3% (E in Table 1)
- As-Built (AB) with relative density 28.6% $\pm$ 0.1% (C in Table 1)
- Chemically Etched (CE) with relative density 29.5% $\pm$ 0.6% (D in Table 1)

For each of these sample conditions, an SN-curve was constructed by testing at least two identical samples at one stress amplitude until failure. The applied loading was chosen such that data was gathered over the fatigue life spectrum between 10^3 - 10^6 cycles. The failure criterion was defined as the moment when a sudden decrease in displacement (1mm/s) occurred. To allow lateral expansion of the samples during loading in compression, a PTFE (polytetrafluorethylene) foil of 0.3 mm thickness was placed between the sample and the hardened compression plates.

SN-curves were first constructed by plotting the global stress as function of the number of cycles to failure. This global stress is calculated by dividing the applied force by the cross sectional area of the porous sample. In a next step, a local stress method developed by Van Hooreweder et al. was used for fatigue life analysis (Van Hooreweder et al. 2017). For every load condition, the maximum local normal tension stress S_1 in the struts was calculated analytically using Equation 1 with local strut force F , strut length L , strut diameter d and strut angle ϑ . The calculated local stress value S_1 was then used to construct SN-curves in which the actual local fatigue behavior is represented. This local stress method for studying the fatigue behavior of porous structures takes the material removal due to chemical etching into account, as described in more detail in (Van Hooreweder et al. 2017).

$$S_1 = F \left(\frac{16L\cos\theta}{\pi d^3} - \frac{4\sin\theta}{\pi d^2} \right) \quad (\text{Eq. 1})$$

Quasi-static mechanical tests were performed using an Instron 5985 machine with a 30kN load cell for the quasi-static compression testing according to ISO 13314. Before testing, the stiffness of the machine frame was measured and this was used for the compliance correction and for an accurate determination of the samples displacement. For sample testing, the compression load was applied with constant strain rate of 0.9mm/min. The test

was stopped at 70% compressive strain. The same sample conditions as for fatigue testing were considered.

From the compressive stress-strain curves the following properties were determined: the maximum stress σ_{max} , the plateau stress σ_{pl} which is calculated as the arithmetic mean of the stresses between 20% and 40% strain, the quasi-elastic gradient E_{QE} which is the gradient of the straight line in the linear deformation region at the beginning of a compression test, and the compressive offset stress σ_{off} which is the compressive stress at 0.2% plastic strain obtained from the quasi-elastic gradient. The offset stress is considered to represent the yield stress σ_y of the porous structures to enable comparison with other studies. In line with other studies, the stresses from quasi-static testing defined above are properties of the porous structure. Hence the yield, plateau and maximum stress values reported above all refer to the virtual stresses acting on the porous structure, i.e. the applied load divided by the cross sectional area of the cylindrical sample.

3. RESULTS

3.1 SURFACE ROUGHNESS

According to the ISO4288:1996 standard (ISO 4288:1996) an arithmetic mean of surface roughness requires a surface length of 12.5 mm. Due to the size of scaffolds this was not possible. Since roughness measurements are being used comparatively and all measures are being performed in the same fashion, the effect of the small test length is assumed to be consistent and therefore can be ignored. The average roughness results can be seen in Figure 6 and Figure 7.

To facilitate visualization of changes in roughness with changes in concentration, Figure 6 shows only the mean roughness value measured. Where required interpolation was performed by assuming a linear function between data points. Figure 6 shows that in general as the concentration of HCl and H₂O₂ increases the roughness of the scaffold exposed to the reagent decreases and that this change begins at a H₂O₂ concentration of 2.5% and an HCl concentration of 22%. This is consistent with the removal of attached particles from the scaffold surface observed using stereo microscopy (Nikon SMZ 745) which was observed to be complete after a 4 minute immersion in a mixture of 18ml HCl (Emsure 37%, Merck), 4ml H₂O₂ (GPR Rectapur 50%, VWR Prolabo) and 3ml of demineralized water. This makes an 8vol% H₂O₂, 27vol% HCl solution. Fresh etchant was prepared for each test. Figure 6 does not show the increase in surface roughness of scaffolds treated with the most concentrated acids, but this can be seen in Figure 7.

Figure 7 shows some of the data used to construct Figure 6 including the spread of results for each test. The results suggest that as the concentration of acid increases the roughness of the treated scaffold decreases. Due to the overlap of the spread of results this cannot be said to be proven, indeed this overlap suggests the change in roughness is negligible, but the trend is consistent with micro-pitting observed under electron-microscopy (SEM) which can be seen in Figure 8.

The microstructure of an etched cross section of an untreated sample (Figure 9) shows that the downfacing sides of the struts are significantly rougher than the upfacing sides. This roughness is compounded by the fact that more partially melted particles stick to the downfacing surface as this part of the structure is scanned by lasers above an open powder

bed. This inhomogeneity in surface properties must be taken into account when evaluating roughness measurements based on optical images. Furthermore any chemical post treatment is expected to be influenced by the local initial roughness.

Table 2 Roughness from optical microscopy images

Treatment	$\bar{\chi}$ Ra (μm)	σ Ra (μm)
Etched 1	26.1	6.8
Etched 2	20.2	6.6
Unetched 1	13.2	3.5
Unetched 2	20.8	6.1

Roughness measurements were repeated with optical microscopy images of scaffold cross sections. This allowed an increase in image and therefore measurement resolution from 4.25 μm per voxel to 1.2 μm per pixel. For optical microscopy images 2 physical cross-sections were used instead of the 3 slices used for X-ray images. To counterbalance the reduced sample space 8 measurements were made per cross-section. The results can be seen in Table 2. These results suggest an increase of mean surface roughness from 20 μm to 28 μm when a scaffold is exposed to the proscribed surface treatment. However once again due to the spread in results the surface roughness change must be assumed to be negligible.

An alternative to the classic Ra measurement is to represent a surface profile's deviation from its average height with a sum of sinusoidal functions. These sinusoidal components can then be separated by wavelength. When etched and unetched components are compared in this way it can be determined whether the difference in roughness is more related to large or small features. This was done at the same time and with the same data as the measurements for Ra using optical microscopy images. These results can be seen in Figure 10 and support the results of the Ra measurements on the optical microscopy images, that the surface roughness of etched and un-etched samples is not different on a statistically significant level.

3.2 FATIGUE RESISTANCE

Fatigue resistance tests were performed on larger scaffolds than those used to measure roughness. The volume of solution was increased for the larger scaffolds to 300ml HCl, 50ml H_2O_2 and 50ml of H_2O as this was observed to achieve comparable results. In both cases a submersion time of four minutes was used.

Figure 11 shows the SN-curves resulting from the global stress method (A) and from the local stress method (B). The global method does not eliminate the effect of the differences in relative density between the three sample conditions. As a result, the fatigue resistance of the samples with high relative density is higher compared to the samples with low relative density and the effect of the chemical etching on the fatigue life is not clearly visible. The local stress method includes the effect of strut diameter in calculating the maximum local stresses and hence the differences in relative densities are taken into account (Van Hooreweder et al. 2017). This can be seen from the failure data of the two as-built sample conditions with different relative densities that approach the same trend in Figure 11 (B). The failure data from the chemically etched samples also follows this trend. This indicates

that the chemical etching treatment does not significantly alter the fatigue performance of the SLM-CoCr samples studied in this work.

During cyclic testing, fluctuating compression-compression loading was applied which normally does not lead to fatigue failure. However, when looking at the fatigue samples as structures, it becomes clear that the struts or beams are actually loaded in a combination of cyclic bending and cyclic axial compression (Van Hooreweder et al. 2017). Therefore the cyclic loading of the structure in compression-compression leads to both compressive and tensile stresses in the struts and these tensile stress components cause the successive fatigue failure of the struts, ultimately leading to failure of the porous sample.

The surface quality is known to have an importance influence on the fatigue behavior especially in the medium-to-high cycle fatigue region 10^5 - 10^8 (Schijve 2001). It is expected that the smooth surface after chemical etching would improve the fatigue life of the SLM CoCr samples in this range. However, chemical etching does not result in improved fatigue strength, as shown in Figure 11.

3.3 COMPRESSION STRENGTH

Figure 12 shows two representative compression curves for all three sample conditions: AB-E with high relative density, AB-E with low relative density, and CE-D. From these curves, the quasi-static material properties were calculated as shown in Table 3. The data shows that both strength and stiffness tend to rise with increasing relative density of the samples, as expected. Apart from this, the general “shape” of the curves is very similar, which indicates that the chemical etching treatment did not significantly change the quasi-static material behavior.

The presented data in Figure 12 corresponds to typical compressive stress-strain behavior of porous ductile metals (Gibson and Ashby 1988, Mustafa et al. 2001). Three regions can be distinguished (Ashby et al. 2000): (I) linear region between ± 0 -5% strain which is related to elastic deformation, (II) “plateau” region between ± 5 -40% strain which is related to the collapsing of pores, and (III) rapid stress increase region from ± 40 % strain which is related to densification and which starts when all pores have collapsed.

Figure 12 also shows that the etched samples behave in a slightly more brittle fashion than non-etched samples. The collapsing of the first pores occurs at 10% compressive strain compared to 15-20% compressive strain for the non-etched samples. The increased brittleness of etched samples could be caused by micro-pitting as seen in Figure 8.

The stress-strain behavior of porous SLM-CoCr samples shown in Figure 12 is much more damped compared to for instance the behavior of porous SLM-Ti6Al4V samples. This is illustrated in Figure 12 where quasi-static data from a similar as-built SLM-Ti6Al4V sample from (Van Hooreweder et al. 2017) is added. For Ti6Al4V samples, deformation in the plateau region (region II) occurs by successive collapsing of unit cell layers along 45° crush bands (Andrews et al. 2001, Van Hooreweder et al. 2017). The stress fluctuates in this region: it increases to a maximum at which one unit cell layer fails, after which the stress will drop

which corresponds to the sudden collapse of that layer. This cyclic process is repeated until all unit cell layers have collapsed. For CoCr samples the sample – and hence the unit cell layers – deforms more uniformly until all pores are closed, indicating that these samples deform more plastically than Ti6Al4V samples. Since the geometry and size of all samples are equal, this means that for the samples used in Figure 12, the ductility of CoCr is higher than the ductility of Ti6Al4V. This leads to two effects:

- Material ductility is often beneficial for the fatigue behavior and so the fatigue performance of CoCr samples might be superior compared to Ti6Al4V samples.
- Previous work has shown that chemical etching improves the fatigue behavior of SLM-Ti6Al4V scaffolds (Van Hooreweder et al. 2017). The high ductility of the CoCr samples, however, also leads to low notch sensitivity, which might minimize the beneficial influence of chemical etching on the fatigue life.

Table 3 Average quasi-static mechanical properties

	E_{QE} [GPa]	σ_{max} [MPa]	σ_y [MPa]	σ_{pl} [MPa]
AB - E (36.1%)	3.43	116.34	73.91	110.39
CE - D (29.5%)	2.32	75.97	53.05	85.27
AB - C (28.6%)	2.22	78.57	50.42	75.00

4. DISCUSSION

In addition to HCl/H₂O₂, solutions of HCl and H₂O₂ are also noted as possible etchants for CoCr alloys (Pyka et al. 2012). Both are preferable to HF based etchants for health and safety reasons. Etchants composed of HCl and HNO₃ were tested but were found to be insufficient for a reaction to the alloy in question. This was confirmed when the surface was examined under stereo-microscope.

The strength of the reaction between CoCr and the chosen HCl and H₂O₂ based etchant was quite violent. Due to the rapid evolution of gas a reaction a vessel of five times the solution volume should be considered as a minimum size when using the proscribed solution and a fume hood is of course obligatory. Further development of the etchant could look to increase the controllability of the reaction in this area.

The maximum amount of time that scaffolds visibly reacted with the HCl/H₂O₂ solution was approximately four minutes. While the surface roughness could decrease if submerged for longer than 4 minutes the change was not significant enough to be visible. A likely explanation is the rapid consumption of H₂O₂ and therefore its effective removal from solution. For this reason a 4 minute immersion was used.

While X μ CT offers the advantage of a full 3D image the resolution of images used to measure surface roughness of scaffolds in this case might rightly be considered inadequate for a true measure of roughness. It is also recognized that a 2D measure of roughness, below the recommended length, on a curved 3D surface could be considered inadequate for a comparison to mechanical properties. The authors recognized these inadequacies so presented three different roughness measurements using two different sampling

techniques, one of which had a resolution close to 1 μm . In the future a 3-dimensional measure of roughness, independent of geometry could improve this step. Despite these concerns, the consistency of the roughness measurements with the fatigue measurements as well as each other gives confidence in the value of those results.

While chemical etching did successfully remove residual particles from the surface of CoCr scaffolds it did not yield a significant change in the fatigue properties as has been observed in other materials that have undergone similar surface treatments. In recent work by Van Hooreweder et al., for instance, SLM Ti6Al4V scaffolds were studied with similar properties: $D=10\text{mm}$, $H=15\text{mm}$, $a=1\text{mm}$, diamond unit cell and relative density 30-40%. For these samples a significant improvement in fatigue strength was noticed after etching compared to as-built samples (Van Hooreweder et al. 2017). Four possible reasons for the observation that the fatigue resistance of scaffolds was not improved by the chemical etching include: (i) the change in surface roughness was insignificant compared to other structural flaws, (ii) etching resulted in particle removal but also in poor surface quality (micro-pitting, see Figure 8), (iii) CoCr parent material has a low notch sensitivity and (iv) the remaining porosity in the struts (see Figure 4) is dominating the fatigue failure.

No large structural flaws were found at the surface of the struts near the nodes where fatigue failure usually initiates due to stress concentrations (Gibson and Ashby 1988, Van Hooreweder et al. 2017), so the effect of hypothesis (i) is presumably limited. Surface pitting was identified in SEM images of the strut surface. Hypothetically this pitting could happen at the same time as removal of existing stress concentrators from the surface thus on balance fatigue resistance could remain unchanged. Hypothesis (ii) would therefore be consistent with observed changes under SEM as well as insignificant changes in R_a after etching. However the effect of the observed micro-pitting is most probably negligible compared to the “staircase-effect” and the “beach marks” between successive solidified melt pools that are present in the as-built condition as observed in Figure 8A. These effects are almost completely removed after etching as shown in Figure 8B.

Due to the ductility of CoCr, illustrated by quasi-static compression data, the scaffolds can be expected to be less notch sensitive than other more brittle materials such as Ti6Al4V (Schijve 2001). Surface roughness and micro-pitting could be considered as “notches” that lead to stress concentrations. However, for a material with a high ductility (such as the CoCr samples studied in this work), the effect of these notches on fatigue life could be small compared with materials with lower ductility (such as the SLM-Ti6Al4V samples studied in (Van Hooreweder et al. 2017)). This would also explain the positive effect of chemical etching on the fatigue life of SLM-Ti6Al4V samples in (Van Hooreweder et al. 2017). In addition the notch sensitivity and internal porosity of the scaffolds was consistent so more likely to explain a consistent fatigue resistance. For these reasons, in the opinion of the authors, the two remaining hypothesis (iii and iv) have the highest probability of explaining the limited effect of chemical etching on fatigue resistance.

Fatigue failure usually initiates from the surface but internal porosity could also serve as a crack initiation site. For the samples studied in this work, large geometrical stress concentrations are present at the surface of the struts near the nodes of the unit cells. This is

due to the diamond unit cell type in which struts are loaded in bending and axial compression (Van Hooreweder et al. 2017). It is therefore expected that for the scaffolds studied in this work, cracks are still initiated from the surface. While (iv) cannot be eliminated the authors therefore come to the conclusion that hypothesis (iii) the low notch sensitivity of CoCr makes etching negligible when considering the fatigue resistance of SLM CoCr scaffold. More research is required to verify this, for instance by applying hot isostatic pressing to the samples to reduce internal porosity before mechanical characterization.

The conclusion then is that while the etchant does remove metal powder particles from the surface, an important step in the production of SLM biomaterials, the chosen etchant has a negligible effect on fatigue resistance. It has been noted that a certain level of surface roughness is ideal for bio integration (Mustafa et al. 2001) so the pitting observed on the scaffold surface could be considered a secondary positive result to the primary positive results of particle removal if the product is intended for use in which osseointegration is a factor.

5. CONCLUSIONS

Etching Selective Laser Melted CoCr scaffolds with an aqueous solution containing 27vol% HCl and 8vol% H₂O₂ removed remnant particles from the scaffolds as required for medical implant surfaces. The solution was observed to produce surface micro-pitting but the surface treatment did not improve nor degrade the fatigue life of the scaffolds tested.

Strength also remained unchanged. That the fatigue life remains unchanged after etching SLM-CoCr scaffolds is surprising in light of other authors' previous work on SLM-Ti6Al4V scaffolds for which etching significantly improves fatigue properties.

The insignificant differences in fatigue strength are consistent with measurements of surface roughness. However this just moves the question one step back. Why the roughness appeared to remain constant, if considering the range of results, or to decrease then increase bi-modally relative to etchant concentration is also inconsistent with other authors' previous work on 3D printed titanium alloy scaffolds. This material specific behavior requires further investigation.

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Figure 1 Schematic of the geometry of the cylindrical porous samples consisting of diamond unit cells

Figure 2 Strut thickness of CoCr scaffolds, A (as-built) and B (etched) (see Table 1)

Figure 3 3D reconstruction of scaffold (A), single reconstruction slide used for R_a measurement (B) and cut-away of 3D reconstruction showing approximate slide position (C). All images were taken on samples from group A.

Figure 4 Microscopy image of cut and mounted scaffold (A) and Longitudinal cross-section of non-etched scaffold (B). Each image is a composite of approximately 20 images, images were taken on samples from group A.

Figure 5 Example of scaffold cross section (group A) with measured surface (red) and mean surface (green)

Figure 6 Approximation by interpolation of relationship between H_2O_2 and HCl concentrations and resultant roughness measurement when using $X\mu CT$ images on samples from group B. The blue surface indicates the minimum concentration for reactants HCl and H_2O_2 needed to affect the roughness at 22 and 2 vol% respectively

Figure 7 Effect of increasing HCl concentration and surface roughness as measured using X μ CT images. Points are the calculated mean value. Error bars are based on standard deviation so the total range of the bars covers two standard deviations of the roughness values measured. H₂O₂ concentration not constant (see Figure 5). Measured on samples from group B.

Figure 8 Unetched (A) and etched (B) scaffold surface under SEM showing particle removal and apparent micro-pitting in the etched material

Figure 9 A longitudinal cross-section along one strut of an untreated sample (group A) . 50x magnification, 1.2 μm per pixel. The microstructure is revealed by electrochemical etching in 10% HCl at 6V.

Figure 10 Surface roughness wavelengths for unetched (group A) and etched (group B) samples. The histograms represent the mean values and the error bars the standard deviation.

Figure 11 SN-curves with failure data of as-built (AB) and chemically etched (CE) samples plotted on a log-log scale using the global (A) and local (B) stress method.

Figure 12 Quasi-static compression data for as-built (AB) and chemically etched (CE) SLM-CoCr samples compared to SLM-Ti6Al4V samples