Highly effective smoothening of 3D-printed metal structures via overpotential electrochemical polishing

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\textbf{ABSTRACT}

High roughness of metal structures made by selective laser melting restricted their extensive applications. A strategy of overpotential electrochemical polishing was developed for effectively smoothening three-dimensional (3D)-printed surfaces, particularly for removing sticking particles. Average surface roughness of 0.18 µm was achieved with a small thickness removed of $\sim 70$ µm through a combination of overpotential and conventional electrochemical polishing. Interestingly, micro-lattices polished with this approach nearly doubled the specific compressive plateau stress and energy absorption over as-printed lattices. Moreover, the success with 316L stainless steel, 4130 steel and AlSi10Mg, indicates the potential of this approach for smoothening other 3D-printed metals.

\textbf{IMPACT STATEMENT}

A highly effective technology to smoothen complex and rough 3D-printed metal surfaces is developed using a novel overpotential electrochemical polishing, which can enhance mechanical and functional properties of 3D-printed metals.

\textbf{Introduction}

Selective laser melting, known as a powerful three-dimensional (3D) manufacturing technology, facilitates direct fabrication of dense and strong 3D metals with almost unlimited flexibility of geometry and complexity \cite{1,2}. However, metal structures made by selective laser melting usually have an extremely rough surface because of the powder-based point-by-point 3D printing process \cite{3}. The issue is more severe for complex structures (lattices, pipes, etc.) with internal features \cite{4,5}. Apart from mechanical properties, the rough surface also affects other functional properties significantly, such as specific energy absorption, corrosion resistance, fluid dynamics and optical properties \cite{6–8}.

Up to now, limited improvement of surface quality has been achieved by optimization of selective laser melting process parameters \cite{9}. The external top surface roughness can be further reduced by in-situ laser re-melting, but this laser re-melting is less effective for external or internal side surfaces \cite{10,11} (see Supplementary Material, and Figs. S1A and S1B for details of various 3D-printed surfaces). Some external side surfaces which are accessible by polishing tools or laser beams can be further smoothened by surface treatments such as mechanical or...
laser polishing. However, these common polishing methods cannot access most internal surfaces, for example, pipes with a high aspect ratio and lattices [12,13]. Hybrid additive and subtractive manufacturing processes have been developed for improving 3D-printed metal surface [14]. However, irregularly-shaped machine waste from subtractive operations (milling/grinding) could hinder powder from spreading properly, and machining after each layer is time-consuming and may also break fine structures. Chemical etching has been explored for polishing structures made by selective laser melting, but its indiscriminate low-contrast removal often results in a significant deviation from the original geometry and dimensions. Deterioration of mechanical properties has also been reported after chemical etching due to morphology change [15].

Electrochemical polishing (ECP) has been widely used for fine polishing of metals, with an initial average surface roughness ($R_a$) on the order of $\sim 1 \mu m$ down to a mirror finish [16,17]. For conventional electrochemical polishing, a relatively low voltage in the limiting-current plateau region is applied [16,18,19]. However, few previous studies and our preliminary results have shown that conventional electrochemical polishing resulted in non-selective and ununiform smoothening/removing for 3D structures made by selective laser melting [15,20] because the as-printed surface is too rough to be addressed. It is therefore in high demand to develop a new strategy to polish complex 3D-printed metal surfaces on the premise of less change to the original structure.

In this work, we have developed a novel polishing process, a combination of overpotential and conventional electrochemical polishing for effective smoothening of 3D-printed side/internal surfaces. Selection of a potential slightly above the current plateau region (overpotential) can achieve a highly selective removal of sticking particles. A further smoothening can be obtained by a subsequent conventional electrochemical polishing. Finally, the $R_a$ can be reduced from $\sim 8 \mu m$ initially to 0.18 $\mu m$ with a small removal thickness of $\sim 70 \mu m$. Importantly, the specific plateau stress and energy absorption of polished micro-lattices were nearly doubled compared with as-printed ones. This smoothened surface is favorable for complex structures in high-end applications, and it breaks through the limitations of current 3D-printed metals.

**Experimental**

**3D Printing of micro-lattices and pipes**

Metal 3D printing was carried out with a SLM® 280HL (SLM Solutions GmbH, Germany). Spherical 316L stainless steel powder (SLM Solutions GmbH, Germany) with an average particle size of $\sim 30 \mu m$, 4130 steel powder (Sandvik Osprey, Sweden) ($\sim 30 \mu m$), and AlSi10Mg powder (SLM Solutions GmbH, Germany) ($\sim 40 \mu m$) were employed for selective laser melting.

**Overpotential electrochemical polishing**

The electrolyte for 316L stainless steel was a mixture of 60 vol.% phosphoric acid (Sigma-Aldrich), 30 vol.% sulfuric acid (Sigma-Aldrich), 0.3 vol.% glycerol (Sigma-Aldrich) and 9.7 vol.% DI water. The overpotential electrochemical polishing experimental setup was shown in Figure S3A.

**Modeling and simulation**

Finite element analysis (FEA) was conducted to study the compressive responses of the lattices with the commercial finite element package Abaqus/Explicit 2017 (Dassault Systèmes). The constitutive material of body-centered-cubic (BCC) lattices was considered isotropic. The BCC lattice structures were modeled using linear tetrahedral elements (C3D4).

**Characterization**

Scanning electron microscopy (SEM) was performed on ZEISS SEM Supra 40. The mechanical properties were evaluated by EZ50, LLOYD INSTRUMENTS. The surface roughness and profile was measured by Form Talysurf PGI 2540 (Tylor Hobson, US). Micro X-ray computed tomography (Micro-XCT) study was carried out by using high-resolution Micro-XCT system Phoenix Nanotom® M (GE Sensing & Inspection Technologies GmbH, Germany). The arithmetical mean height of the scale limited surface (Sa) of BCC lattices was calculated by VG Studio software (Volume Graphics GmbH, Germany) according to the Micro-XCT scans [21].

**Electrochemical measurements**

The electrochemical experiments were performed with the VMP3 electrochemical workstation (Bio-Logic Science Instruments, France). The anodic electrode was used as the working electrode, a 316L stainless steel plate was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. Anodic polarization curves were measured at scan rate of 10 mV s $^{-1}$. Electrochemical impedance spectroscopy (EIS) measurements of the samples were carried out on the above three electrode systems. The frequency range
Results and discussion

Figure 1 shows the schematic diagram of 3D-printed surfaces and proposed polishing strategy. Regarding the surfaces made by selective laser melting, there are two types of surface profiles. The Type I surface profile is formed by balling and staircases, as shown in Figure 1(A–C), with more details given in Figs. S1C–S1E. It has a typical profile width of 100–200 μm and a profile height of 50–100 μm (see Fig. S2). The Type I surface profile strongly depends on selective laser melting process parameters. The Type II surface profile refers to partially melted metal particles sticking on the as-printed side surface, with a smaller profile width of 40–100 μm and a profile height of 20–50 μm, as shown in Figure 1(C). The co-existence of Type I and Type II surface profiles on as-printed surface makes it too complicated to be polished by conventional methods. Figure 1(D) shows our strategy: Step 1—removal of sticking particles (Type II surface profile) using overpotential electrochemical polishing (see Figs. S3 and S4); Step 2—further smoothening by conventional electrochemical polishing. Through this combination, smooth and shiny surfaces (internal and external) of complex 3D-printed metal structures (Figure 1(E)) were successfully achieved (vide infra).

We took 316L stainless steel as a prototype material for this study. Note that the as-printed 316L stainless steel plate has a typical rough side surface, with a Ra of ∼8 μm (as shown in Figure 2(A)). Figure 2 shows the anodic polarization curve of as-printed 316L stainless steel plate sample. A limiting-current plateau appeared in the potential interval between 1.5 and 1.9 V. This region is usually chosen for conventional electrochemical polishing. More frequently, conventional electrochemical polishing is performed with a potential in the middle of the current plateau region [18,19,22]. Here, we have investigated the resultant surface morphological changes’ dependence on potential. There was little change when the applied potential was below 1.5 V because this is in the corrosion reaction region with a reduced polishing rate. Scanning electron microscopy (SEM) images (Figure 2(B–F)) show surface morphology after electrochemical polishing with different potentials applied from 1.5–2.2 V. After 20 min of polishing, sticking particles can still be seen clearly if the potential was in the current plateau region (1.5–1.9 V), as shown in Figure 2(B–D). In contrast, polishing with a slight overpotential (2.0–2.1 V), defined as overpotential electrochemical polishing (OECP), can achieve effective smoothening effect, as sticking particles (Type II surface profile) were removed and the best Ra value (1.1 μm) among different applied potentials was obtained (Figure 2(E)). The mechanisms and characteristics of overpotential electrochemical polishing were explored in Fig. S3. Further increases in potential to higher than 2.2 V caused excessive and nonuniform polishing (Figure 2(F)), as uncontrollable dissolution played a dominant role in this region.

Another important parameter is temperature. As shown in Fig. S4, a lower temperature ( < 50°C) has little effect on the removal of sticking particles. The optimum temperature range is 50–60°C. A further increase in temperature could lead to uncontrollable polishing. A phosphoric-sulfuric acid mixture has been widely used in electrochemical polishing of stainless steels [18]. We have investigated the effects of the ratio of these two acids in this study. The volume ratio of 2:1 of phosphoric to sulfuric acid gave the best surface roughness after overpotential electrochemical polishing for 20 min (see Fig. S4). Therefore, phosphoric-sulfuric mixture acid with a ratio of 2:1 and an elevated temperature of 50°C were used for the rest of this work.

Type I surface profile depends on printing process parameters. Fig. S5A shows a relatively higher roughness because large hatch spacing and powder layer thickness were chosen. After overpotential electrochemical polishing for 40 min, some steps still can be seen in Fig. S5B. When the reduced hatch spacing and powder layer thickness were used (Fig. S5C), a much smoother surface with a Ra of 0.23 μm was obtained after overpotential electrochemical polishing for 40 min (Fig. S5D). Thus, a reduction of the Type I surface profile to close to the Type II surface profile in the printing stage is beneficial for more effective smoothening.

Figure 3(A) shows side surface roughness Ra and removal thickness as a function of polishing time in overpotential electrochemical polishing. The roughness Ra decreases quickly in the first 30 min, reducing it from ∼8 μm to below 0.8 μm (a general assembly roughness for most engineering applications) [23]. The Ra can be further smoothened to 0.18 μm with a total polishing time of over 60 min. To maintain the original structure, material removal should be minimized. It can be seen that the Ra can reach ∼0.6 μm with a removal thickness of only ∼45 μm. This shows significantly selective removal of sticking particles (Type II surface profile) during overpotential electrochemical polishing, considering the particle size of 20–50 μm. Furthermore, a combination of novel overpotential electrochemical polishing and conventional electrochemical polishing was developed for more effective smoothening of the as-printed surface. Our combined polishing concept and experimental results were illustrated in Figure 3(B). After overpotential...
Figure 1. Schematic representation of three-dimensional printed stainless-steel surfaces and surface profiles. (A) 3D-printed surfaces derived from powder-based point-by-point selective laser melting process. (B) As-printed top surface. (C) As-printed side surface, which can be divided into Type I and Type II surface profiles. (D) Strategy for smoothening of as-printed side surface, a combination of overpotential electrochemical polishing (OECP) and electrochemical polishing (ECP). (E) As-printed 3D structures with complex side surfaces before and after smoothening by a combination of overpotential electrochemical polishing and electrochemical polishing.

Electrochemical polishing for 20 min, the potential was reduced to a typical value of 1.7 V to conduct a conventional electrochemical polishing for another 20 min, and a $R_d$ of 0.18 μm with a small removal thickness of $\sim 70$ μm was achieved.

One of the major advantages of 3D printing is to fabricate geometrically-complex structures, such as lattice structure with complicated internal features. Figure 4 shows as-printed and polished 316L stainless steel micro-scale body-centered-cubic (BCC) lattices made by selective laser melting. Very rough surfaces were found in the as-printed lattices (see Figure 4(A)). After conventional electrochemical polishing for 40 min, lattice surfaces are still rough and particles are still visible, even if some struts were broken because of excessive and nonuniform polishing (Figure 4(B)). This has indicated that conventional electrochemical polishing cannot be used for smoothening complex or fine-featured 3D structures made by selective laser melting (Fig. S6). In contrast, a smooth surface appears after...
Figure 2. Comparison of polishing efficacy and quality of different potentials applied to as-printed side surface with the same polishing time of 20 min. (A) Scanning electron microscopy (SEM) image of the side surface of as-printed 316L stainless steel plate. (B–F) SEM images of side surfaces after polishing with the potentials of 1.5, 1.7, 1.9, 2.1 and 2.2 V, respectively. (E) A smooth surface was achieved. Scale bars, 100 μm.

Figure 3. Evaluation of surface roughness and removal thickness during overpotential electrochemical polishing (OECP) and the combination of overpotential electrochemical polishing (OECP) and electrochemical polishing (ECP) processes. (A) The conventional average surface roughness (Ra) and removal thickness as a function of polishing time in f overpotential electrochemical polishing process. (B) Surface morphology and the corresponding roughness and removal thickness in a combination of overpotential electrochemical polishing and electrochemical polishing process.

overpotential electrochemical polishing for 40 min, as shown in Figure 4(C). The lattice struts become thinner, and a reduction in diameter of ∼150 μm can result in smooth surfaces by a single overpotential electrochemical polishing. When a combination of overpotential electrochemical polishing and electrochemical polishing process was applied, the diameter reduction can be reduced to 110–120 μm (Fig. S7).

Figure 5(A,B) showed as-printed and polished lattices under micro X-ray computed tomography (Micro-XCT). The results revealed that a uniform and smooth surface throughout the whole lattices were achieved by a
Figure 4. Smoothening of 3D-printed body-centered-cubic (BCC) lattice surface by conventional electrochemical polishing (ECP) vs. novel overpotential electrochemical polishing (OECP). (A) As-printed rough lattice surface with sticking particles. (B) Morphology of lattice surface after conventional electrochemical polishing for 40 min, fine struts are broken during electrochemical polishing process. (C) Morphology of lattice surface after novel overpotential electrochemical polishing for 40 min, smooth and uniform struts are achieved.

A combination of overpotential electrochemical polishing and electrochemical polishing process. The arithmetical mean height of the scale limited surface (Sa) of the lattice struts was reduced from ∼9 μm to below ∼0.8 μm. As a demonstration, we studied the influence of surface polishing on compression properties of BCC lattices in Figure 5(C,D). The experimental and numerical stress–strain curves of as-printed, polished (via a combination of overpotential electrochemical polishing and electrochemical polishing) and an ideal BCC lattices with similar relative densities (∼0.18) were comparatively studied in Figure 5(C). Interestingly, polished lattice structure exhibited much higher specific compressive plateau stress and compressive modulus, which was ∼1.9 times and ∼1.3 times that of as-printed lattices, respectively. Again, the polished lattices significantly outperformed as-printed lattices in specific energy absorption, on the order of ∼1.8 times. Note that polished lattices displayed smaller stress fluctuations in the plateau region than the as-printed one. Moreover, the experimental stress–strain curve, deformations and failure mechanisms of polished BCC lattices are very close to the predicted results from finite element analyses (FEA) for ideal BCC lattices (uniform and smooth structure without any defects). All of these mechanical enhancements derive from the removal of surface defects and useless weight of as-printed BCC lattices through a combination of overpotential electrochemical polishing and electrochemical polishing. More detailed FEA information was provided in experimental, and Fig. S8.

In order to study the feasibility of the proposed morphology for other internal structures, we tested two pipe structures, namely a curved pipe with constant-diameter and variable-diameter pipe. We have developed methods for polishing these internal pipe surfaces with the assistance of tailored 3D-printed electrodes, as illustrated in Figs. S9A and S9B. Satisfactory polishing results of pipes can be obtained (Fig. S9C). Note that selective
Figure 5. Three-dimensional surface models of BCC lattice structures imaged using micro X-ray computed tomography (Micro-XCT) and compression experiments and simulations. (A) 3D rendered volume of as-printed BCC lattices, very rough struts with large numbers of sticking particles. (B) 3D rendered volume of polished BCC lattices, smooth and uniform lattices are obtained by a combination of overpotential electrochemical polishing (20 min) and electrochemical polishing (20 min). (C) Macropscopic compression stress–strain curves obtained from the experimental tests (as-printed and polished lattices), and finite element analyses (FEA) (ideal lattices with smooth surface) for BCC lattices with similar relative densities. (D) FEA predicted stress plots (ideal lattices) and experimental deformations (polished lattices) at given strains.

laser melting is also a powerful tool to fabricate custom-shape electrodes which can fit well in different internal structures, as depicted in Fig. S9.

To confirm that our polishing method is widely relevant, we have also studied the polishing effects on other metals. Similar results of good smoothening effect on 3D-printed 4130 steel and AlSi10Mg have been observed (see Fig. S10). Our study has shown that the combination of overpotential electrochemical polishing and electrochemical polishing can achieve high-quality surface smoothening for different metal alloys with the choice of a suitable electrolyte.

Conclusions

We have successfully developed a strategy to smoothen rough 3D structures made by selective laser melting. The overpotential electrochemical polishing at an elevated temperature (50–60°C) with a suitable electrolyte can effectively and selectively remove sticking particles (Type II Surface Profile). The combination of overpotential electrochemical polishing and electrochemical polishing can achieve a good roughness $R_a$ of 0.18 μm from $\sim$ 8 μm initially with a small removal thickness of $\sim$ 70 μm. With the help of tailored electrodes fabricated by selective laser
melting, controllable and efficient smoothing of internal surfaces can be achieved for complex curved pipes. This work also demonstrates the capability of uniformly smoothing fine-featured micro-BCC lattices. Importantly, the specific compressive plateau stress and energy absorption of polished lattices are nearly doubled compared with as-printed ones. Moreover, the success of 4130 steel and AlSi10Mg has indicated that this strategy could be applied to other metals, highlighting that our over-potential electrochemical polishing method is broadly practical. Ultimately, the breakthroughs achieved in this development of effectively smoothing geometrically-complex 3D-printed metals with internal structures, can accelerate broad adoption of metal 3D printing and enabling more innovations and possibilities in high-performance and smooth-surfaced metals related functional applications.

Disclosure statement
No potential conflict of interest was reported by the authors.

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