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# Investigation on the microstructure, mechanical property and corrosion behavior of the selective laser melted CoCrW alloy for dental application

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ABSTRACT

In this study, an experimental investigation on fabricating Ni-free CoCrW alloys by selective laser melting (SLM) for dental application was conducted in terms of microstructure, hardness, mechanical property, electrochemical behavior, and metal release; and line and island scanning strategy were applied to determine whether these strategies are able to obtain expected CoCrW parts. The XRD revealed that the γ-phase and ε-phase coexisted in the as-SLM CoCrW alloys; The OM and SEM images showed that the microstructure of CoCrW alloys appeared square-like pattern with the fine cellular dendrites at the borders; tensile test suggested that the difference of mechanical properties of line- and island-formed specimens was very small; whilst the outcomes from the electrochemical and metal release tests indicated that the island-formed alloys showed slightly better corrosion resistance than line-formed ones in PBS and Hanks solutions. Considering that the mechanical properties and corrosion resistance of line-formed and island-formed specimens meet the standards of ISO 22674:2006 and EN ISO 10271, CoCrW dental alloys can be successfully fabricated by line and island scanning strategies in the SLM process.



## 1. Introduction

Cobalt–chromium based alloys have been widely used in various orthopedic implants such as artificial hip, knee joints and dentistry because of their excellent mechanical properties, high corrosion resistance, and good biocompatibility [1]. For dental application, cobalt–chromium based dental alloys are required to have yield stresses higher than the standard ISO 22674:2006 of 500 MPa. In recent years, improving the mechanical properties of cobalt–chromium based dental alloys therefore has been extensively conducted [2–4]. On the other hand, materials used in dental applications should consist of small grains. This is because chipping failure will occur in machined components with coarse grain structures as consequence of reducing the accuracy of the marginal fit of restorations [5]. Because the Ni can cause skin allergies or cancer in living organisms [3,6], note that novel Ni-free CoCrW has been extensively studied because of their excellent biocompatibility and strong bonding strengths of metal-porcelain, which has high potential for dental applications [7]. Yamanaka et al. [8] prepared Co–29Cr–9W cast alloys with carbon concentrations in the range 0.01–0.27 mass%. The effects of carbon concentration on the microstructures and tensile properties of the Ni-free Co–29Cr–9W cast alloys used in dental applications were reported. Meanwhile, Yamanaka et al. also investigated the effects of nitrogen on the high-temperature deformation and microstructure of biomedical Ni-free CoCrW alloys during the process of hot deformation. The main conclusion of their work was that the solute segregation and resulting carbide precipitation at the grain boundaries were promoted by increased carbon concentrations and were considered as the origin of such grain refinement [5].

In general, dental restorations are fabricated by casting and computer-aided manufacturing technologies. However, cast cobalt–chromium based alloys generally have large grains and exist quite non-homogeneous microstructure and solidification defects, which result in inadequate mechanical properties and inhomogeneous material quality. Therefore SLM technique, a kind of additive manufacturing method that fabricates metal products directly from CAD data in an additive layer-by-layer manner by selectively fusing together metal powder, has been applied in prosthetic dentistry to construct individual restorations with special anatomical characteristics and complex geometry for patients [9,10]. Basic research on cobalt–chromium based alloys for dental applications has been reported using the SLM process [11,12]. As suggested by a previous study that CoCr alloys formed by SLM existed higher corrosion resistance, lower metal release, and lower cell proliferation compared with the cast CoCr alloys. This was due to the formation of fine microstructure with cellular dendrites in as-SLM CoCr alloys during the very high rapid solidification [13]. According to Takaichi et al. [4], dense parts could be obtained and existed better mechanical property and lower amounts of metal release when input

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energy of laser scan is increased more. Obviously, optimization of process parameters, such as scanning speed, laser power, scanning strategies etc., for the fabrication of CoCr alloy is very important, which can affect their microstructure and properties [14]. Among these processing parameters, most concerns of scanning strategies focus on the line scanning strategy that laser moves in bidirectional or unidirectional way across part surfaces [15,16] illustrated in Fig. 1a–c. Actually, due to high local heat input in a short time during the SLM process, the part experiences residual stresses, which can introduce deformation, initiate cracks, even accuracy problem. Additionally, it was reported by Kruth et al. [17], who investigated the influence of vector length in the x-direction on curling of Ti–6Al–4V test part, that the residual stresses decreased when lower vector lengths were applied. In view of this, note that island scanning strategy is recently used to reduce the thermal residual stresses by shortening the individual tracks and dividing each layer into a number of smaller islands [18]. These smaller islands then are randomly scanned in an attempt to produce a more even heat distribution as a consequence of decreasing the residual stresses. The vectors in the neighboring islands are perpendicular to each other. In the subsequent layer, the island is shifted by 1 mm in both the X and Y directions, seen in Fig. 1d–f. The patented process allows solid and large-volume components to be generated with low warping [19]. So far some works have been performed to determine the relationship between the island strategy and properties of selective laser melted specimens [20]. Thijs et al. [21] applied line and island scanning strategies to investigate the microstructure and controllable texture of as-SLM AlSi10Mg parts. Kruth et al. [22] used island scanning strategies with different island sizes to measure the residual stresses of maraging steel. However, they suggested that the size of the islands did not seem to influence the residual stresses.

In contrast with the relatively large body of published works on CoCrMo and CoCrW formed by traditional processes, there is rather limited information on the microstructure, mechanical property, and corrosion resistance evaluations of the CoCrW alloy fabricated by SLM. In this study, CoCrW alloys were fabricated by selective laser melting using line and island scanning strategies to identify whether these parameters are able to obtain expected CoCrW parts for dental applications. The line and island-formed CoCrW alloys were also evaluated in terms of microstructure, hardness, mechanical property, electrochemical behavior, and metal release.

## 2. Experimental detail

### 2.1. Materials and sample preparation

The commercial CoCrW alloy powders were prepared for this study. The particle size distribution is 10–45 μm. The chemical compositions are listed in Table 1. Based on the supplier information, the density of the CoCrW alloy is 8.6 g/cm$^3$.

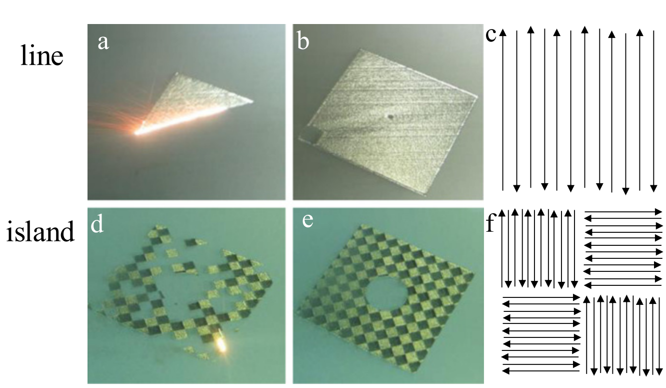


**Fig. 1.** The illustration of the line scanning strategy (a–c) and island scanning strategy (d–f).

The samples were fabricated by the SLM technique (Mlab-R, CONCEPTLAER, Germany). Two kinds of laser scanning strategies, i.e., line scanning and island scanning strategy, were applied for the fabrication of selective laser melted CoCrW alloys, as illustrated in Fig. 1a–f. The detail processing parameters are listed Table 2.

### 2.2. Microstructural observation and phase analysis

Microstructural observation was carried out using optical microscope (Axio Vert.A1, ZEISS) and scanning electron microscope (SEM, JSM-6700F). Phase identification was studied by X-ray diffractometer (XRD, D/MAX-2500PC) with CuK$_\alpha$ radiation. Specimen preparation was firstly mechanically polished, and then etched in HCl for 7 h [14].

### 2.3. Mechanical property characterization

Tensile tests were performed on a universal testing machine (MTS E45.105) at room temperature, with an initial strain rate of 2 mm/s. The schematic diagram of tensile specimen is shown in Fig. 2. Fractography were examined by using SEM (SEM, JSM-6700F). Vickers hardness (HV) of the specimens was also carried out using the hardness tester (HX-1000TM), with a load of 100 gf and a dwell time of 12 s. The density of the samples with the dimension of 10 × 10 × 10 mm was measured by applying Archimedes' principle.

### 2.4. Electrochemical test

Electrochemical test was conducted to evaluate the corrosion resistance in the PBS and Hanks solution at 37 °C. A three-electrode cell was used for the electrochemical measurements. The counter electrode was made of platinum and a saturated calomel electrode (SCE) was used as the reference electrode. The sample with an exposed area of 1 cm$^2$ was taken as the working electrode. The polarization scan was started from anodic region from 250 mV below open circuit potential at a constant voltage scan rate of 0.5 mV/s.

### 2.5. Immersion test

The static immersion test was performed in accordance with the currently specified EN ISO 10271 standard for metallic biomaterials. Samples with the dimensions of Φ10 × 30 mm were fabricated by SLM. Prior to performing this study, the samples were ground with waterproof emery paper to 1200 grit under running water, then ultrasonically cleaned in acetone for 15 min, rinsed in distilled water and finally dried at room temperature. The static immersion tests were conducted using PBS and Hank's solutions, respectively. A 12.56 ml of each solution was poured into the polypropylene bottles each containing a plate specimen. All the sealed bottles were placed inside an incubator at 37 °C for 7 d. The concentrations of various metals released into solution were determined in ppb (mg/ml) by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Ultima2).

### 2.6. Statistical analysis

The SPSS15.0 statistical software package was used for data analysis. $P > 0.05$ was considered as no statistically significant difference.

## 3. Results

### 3.1. XRD study

Fig. 3 shows the XRD patterns of the unpolished top-view of the line-formed and island alloys. As can be seen, both CoCrW alloys exhibit duplex phases of γ (fcc) and ε (hcp) phase. Interestingly, the island-formed alloy exhibits much higher diffraction intensity assigned to ε phase compared with the line-formed alloy.