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Structural characterization of biomedical Co–Cr–Mo components produced by direct metal laser sintering

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ABSTRACT

Direct metal laser sintering (DMLS) is a technique to manufacture complex functional mechanical parts from a computer-aided design (CAD) model. Usually, the mechanical components produced by this procedure show higher residual porosity and poorer mechanical properties than those obtained by conventional manufacturing techniques.

In this work, a Co–Cr–Mo alloy produced by DMLS with a composition suitable for biomedical applications was submitted to hardness measurements and structural characterization. The alloy showed a hardness value remarkably higher than those commonly obtained for the same cast or wrought alloys. In order to clarify the origin of this unexpected result, the sample microstructure was investigated by X-ray diffraction (XRD), electron microscopy (SEM and TEM) and energy dispersive microanalysis (EDX). For the first time, a homogeneous microstructure comprised of an intricate network of thin ε (hcp)-lamellae distributed inside a γ (fcc) phase was observed. The ε-lamellae grown on the $\{111\}_\gamma$ planes limit the dislocation slip inside the γ (fcc) phase, causing the measured hardness increase. The results suggest possible innovative applications of the DMLS technique to the production of mechanical parts in the medical and dental fields.

1. Introduction

Nowadays, a new class of manufacturing methods is becoming increasingly important for the production of biomedical devices. Among them, novel methods based on additive manufacturing (AM), assisted by computer-aided design/computer-aided manufacturing (CAD/CAM), allow the production of intricate mechanical parts [1–4].

Direct metal laser sintering (DMLS) is an AM process that uses the heat of a solid state laser to sinter metal powder particles [5]. In this case, a distribution mechanism pre-places successive layers of powder on a suitable substrate, while a laser beam controlled by a scanning system locally sinters the powder in accordance with the CAD model [6]. This technology, like other AM procedures, is highly rewarding in medicine where a high degree of personalization is required [7–9]. Prosthetic applications are particularly well suited for processing by means of DMLS due to their complex geometry, low volume and strong individualization [10]. Furthermore, the manufacturing of multiple unique parts in a single production run enables extensive customization with a strong reduction of manual operation leading to higher repeatability and good savings in money and delivery times.

Cobalt-based alloys were extensively used in cast and hard facing forms over the past twenty years because of their corrosion and wear resistance, biocompatibility and excellent strength and toughness at high temperature [11]. Typical applications of the Co-based alloys involved both the biomedical and the metallurgical fields [12,13].

From a structural point of view, cobalt is characterized by a ε (hcp) low temperature phase and a γ (fcc) phase at higher temperature. Addition of chromium improves the corrosion and the oxidation resistance of the alloy, as well as its hardness, ductility and wear resistance through carbide formation. Molybdenum improves the corrosion resistance and acts as a solid-solution strengthener by forming the Co_3Mo (hcp) intermetallic compound [14].

Cast alloys with a Cr content ranging from 19 wt.% to 30 wt.% and a Mo content in the range 5–10 wt.% were considered for biomedical applications and for many years these compositions were used to produce medical implants such as hips, knees, ankles and bone plates [15].

Although in the past few years, several AM techniques were applied to produce biocompatible Co-based alloys, only in few cases a deep microstructural characterization of the sintered components were

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performed. In particular, Gaytan et al. reported on the microstructure and the mechanical properties of Co-based prototypes produced by electron beam melting. In this study, they found high hardness values attributed to the formation of an ordinate array of metal carbides [16]. Meacock et al. investigated the microstructure and the mechanical properties of a biomedical Co–Cr–Mo alloy produced by laser powder microdeposition [17]. They observed a homogenous microstructure comprised of fine cellular dendrites and measured an average hardness value of 460 HV_{02}, well higher than the typical values obtained by other fabrication processes. From these results, they concluded that the fine morphology is responsible of the significantly increased hardness value.

Few other papers deal with the possibility of producing medical parts of a Co–Cr–Mo alloy by the DMLS technique, but it is worth to note that none of them reports on the correlation of the sample microstructure to the mechanical properties of the final components as well as the detailed transmission electron microscopy analyses [18–21].

The mechanical properties of the sintered components are strictly linked to the sample microstructure and are one of the major aspects connected to the practical applications of the AM procedures. Usually, objects produced by metal powder sintering show poorer mechanical properties than those produced by conventional procedures. This behavior is mainly due to the fact that DMLS, depending on the laser energy density employed, involves a partial or total melting of the powder. Therefore, the products made by DMLS could show high surface roughness, porosity (in certain cases even lack of densification), heterogeneous microstructure and thermal residual stresses that may give rise to poor mechanical properties [22].

In this paper, metallic components of a biocompatible Co–Cr–Mo alloy produced by the DMLS technique were deeply investigated in order to correlate their hardness behavior to the corresponding microstructure. To this aim, hardness measurements, X-ray diffraction (XRD) analysis, electron microscopy (SEM, TEM) observations and energy dispersive microanalysis (EDX) were performed on the samples. Results evidenced a surprisingly high hardness value of the investigated Co–Cr–Mo alloy in comparison of the hardness values commonly reported in literature for similar compositions. This unexpected result was attributed to the peculiar microstructure observed in the analyzed samples, that, to our knowledge, was never reported before.

2. Materials and methods

2.1. Material composition and sintering parameters

Specimens were prepared by direct metal laser sintering using a Yb (ytterbium) fiber laser system (EOSINT-M270) operating with the standard deposition parameters reported in Table 1.

A Co–Cr–Mo alloy powder (EOS Cobalt/Chrome SP2) with the nominal composition (in wt.%) Co 63.8, Cr 24.7, Mo 5.1, W 5.4, and Si 1.0, was used as raw material. The powder is free of Ni, Be and Cd according to EN ISO 22674. The nominal composition was provided by the manufacturer (EOS GmbH Electro Optical Systems). The powder is the EOS Cobalt/Chrome SP2 cobalt based metal ceramic alloy intended for production of Porcelain-Fused to Metal (PFM) dental restorations (crowns, bridges, etc.) in EOSINT M 270 standard installation mode. The powder is class IIa medical device in accordance with annex IX rule 8 of the MDD 93/42/EEC. Composition corresponds to “type 4” CoCr dental material according to EN ISO 22674.

Table 1
Parameters used for DMLS.

Laser power	200 W
Laser spot diameter	0.200 mm
Scan speed	Up to 7.0 m/s
Building speed	2–20 mm^3/s
Layer thickness	0.020 mm
Protective atmosphere	Max 1.5% oxygen

Rectangular parallelepipeds with size 250 mm × 4 mm and a thickness of 6 mm were sintered by using the parameters reported in Table 1. In order to minimize anisotropy, each layer was built with the laser scanning along a specific direction. Layer-by-layer the scanning direction was rotated by 25° with respect to the previous one.

2.2. Hardness measurements

Hardness tests were performed on the sintered samples using the Rockwell scale C (specifications ISO 4498: Sintered metal materials, excluding hard metals — determination of apparent hardness and microhardness). Measurements were obtained averaging five indentations following ISO 6508: Rockwell hardness test.

2.3. Structural characterization

Structural and microstructural characterizations were carried out by X-ray diffraction (XRD), scanning (SEM) and transmission (TEM) electron microscopy techniques.

XRD measurements were performed by a Bruker D8 Advance diffractometer operating with a Cu-Kα radiation source at V = 40 kV and I = 40 mA in the angular range 2θ = 10–90°.

SEM analyses were carried out by a ZEISS SUPRA 40 microscope equipped with a Bruker Quantax energy dispersive X-ray microanalysis (EDX). Observations were performed on both the as-received metallic powder and cross-sectioned sintered samples. Before observations, sample surfaces were prepared using a conventional metallographic procedure and electrochemically etched in the following conditions: HCl 0.1 M, 2 V, 2 min.

TEM analyses were carried out by a Philips CM200 electron microscope operating at 200 kV and by a JEOL JEM-2010 ARP microscope equipped with an Oxford Inca energy dispersive X-ray microanalysis (EDX). For TEM observations, samples were prepared by the conventional thinning procedure consisting of mechanical polishing by grinding papers, diamond pastes and a dimple grinder. Final thinning was carried out by an ion beam system (Gatan PIPS) using Ar ions at 5 kV.

3. Results

3.1. Hardness

The average Rockwell C hardness (HRC) value measured for the laser sintered samples is 47 HRC, a very high value considering that the usual range for cast Co–Cr–Mo alloys is from 25 to 35 HRC.

3.2. X-ray diffraction (XRD)

X-ray diffraction measurements were performed on both the Co–Cr–Mo powder used as raw material for the DMLS process and on the different regions of the sintered samples (Fig. 1).

Fig. 1a reports the XRD pattern of the as-received metallic powder. All the visible peaks can be attributed to the cubic cobalt phase, commonly referred to as γ phase. The γ phase has a face centered cubic (fcc) lattice with a nominal parameter a = 0.35447 nm (ICDD card n. 15-806). For the alloy under study, the best fit performed by using the three diffraction peaks of Fig. 1a provides a lattice parameter value a = 0.3586 nm, in close agreement with the values reported in literature for alloys of similar composition [23].

The XRD pattern of the sintered sample is shown in Fig. 1b. The most intense and well-defined peaks are a result of the simultaneous presence of both γ and ε cobalt phases, as indicated in Fig. 1b where each diffraction peak is indexed with the name of the corresponding Co phase. A double indexation is reported for the most intense peak at 2θ = 43.94° and the peak at 2θ = 75.09° because of the superposition of the reflections due to the ε and γ phases. The ε phase has a hexagonal close packed (hcp) lattice with nominal parameters a = 0.25031 nm and