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Microstructure and wear properties of LENS® deposited medical grade CoCrMo

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Abstract There is a growing interest in metal-on-metal bearing surfaces for orthopedic implants. Although some success has been achieved in applications like hip implants which involve a large contact area, non-conforming joints, such as knees, have proved more difficult. The current work examines the applicability of a novel additive manufacturing process, Laser Engineered Net Shaping (LENS®, the registered trademark and service mark of Sandia National Laboratories and Sandia Corporation), for producing CoCrMo implants. A series of experiments were conducted to determine the optimum parameters for deposition of CoCrMo. Microstructural studies, hardness tests, and dry sand/rubber wheel abrasive wear tests were conducted on the LENS® deposits. The results showed that metallurgically sound deposits can be produced using the LENS® process under optimized conditions. The hardness of the LENS® deposited CoCrMo was found to be comparable to that of standard CoCrMo wrought material; however, wear tests indicated that LENS® deposits were considerably less resistant to abrasive wear than wrought CoCrMo. The reasons for this behaviour are discussed based on microstructural observations.

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Introduction

Polyethylene-on-CoCrMo bearing surfaces are currently being widely used in knee and hip total joint replacements due to the forgiving nature of the combination to the individual biomechanical nuances of joint recipients. Studies, however, show that, although polyethylene is biologically inert in the body as a whole, microscopic particles of polyethylene resulting from years of wear can possibly be toxic if encountered in large amounts and lead to osteolysis [1–3]. This has led to a growing interest in metal-on-metal bearing surfaces for implants, especially in applications involving a large contact area [4, 5]. A number of metal-on-metal hip implants survived more than 25 years with low wear rates and minimal osteolysis [6].

Cobalt-based alloys are widely used in biomedical applications that require wear and/or corrosion resistance. CoCrMo is the hardest known biocompatible metal alloy with good tensile and fatigue properties [7]. The material has a high corrosion resistance mainly due to the high chromium content that forms a thin passive and tenacious chromium oxide layer protecting the underlying matrix material. These characteristics make it an ideal candidate for metal-on-metal bearing surfaces in orthopedic implants. CoCrMo derives its wear resistance from carbide particle precipitates. Its wear resistance is known to be strongly dependent on volume fraction, size, shape, and distribution of the carbide particles [8]. Another important microstructural consideration is grain size. A fine grain size is desirable in CoCrMo implants for superior tensile and fatigue properties.

The specific manufacturing process used to manufacture CoCrMo implants strongly influences the microstructural characteristics and, therefore, should be carefully controlled to attain the desired properties. Investment casting has traditionally been used to manufacture prosthetic devices in

CoCrMo. However, implant devices manufactured from wrought CoCrMo feedstock though forging and machining processes have increasingly been used in recent years. Wrought CoCrMo implants exhibit a finer grain size with more optimum carbide microstructure and can be finished to a better surface finish than cast CoCrMo materials, and therefore exhibit superior service performance [7, 9].

Laser Engineered Net Shaping (LENS®), a novel additive manufacturing process originally developed by Sandia National Laboratories, is a candidate process for fabrication of biomedical implants. The process has several advantages over conventional manufacturing techniques, including: (i) fully dense end-use metallic components can be rapidly produced without any tooling, molds or dies directly from a Computer Aided Design (CAD) model, (ii) individually customized products can be produced based on digitally input data, (iii) parts can be fabricated from materials that are difficult to process using conventional techniques, (iv) the process allows for precise control of local composition and microstructural features making it possible to produce parts from functionally graded materials, multiple materials and/or composites, and (v) minimal material waste.

A schematic of LENS® is shown in Fig. 1. Initially, a three-dimensional (CAD) model of the component to be built is generated and a computer program slices the model into a number of horizontal cross-sections or layers. These cross-sections are systematically created from bottom to top producing a three-dimensional object. The deposition process begins with directing a focused Nd-YAG laser beam onto a substrate placed on the build platform capable of computer-controlled motion. The laser generates a small molten pool (typically 0.25–1 mm in diameter and 0.1–0.5 mm in depth) on the substrate. Precise amounts of powdered material is injected directly into the melt pool using a powder feeder. The molten pool solidifies rapidly as the laser beam moves away, forming a thin track of solidified metal welded to the material below along the line of laser scanning. A layer is generated by a number of consecutive overlapping tracks. After each layer is formed, the laser head, along with the powder delivery nozzle, moves upward by one layer thickness and the subsequent layer is generated. This process is repeated until the part is complete. The deposition process occurs inside an enclosed chamber filled with argon to prevent oxidation of the liquid metal. The part building process is fully automatic and can run unattended. Although the deposition nozzle utilized for our experiments is aligned along the *z*-axis, 5-axis deposition upgrades are available which enable layers to be deposited on complex contours rather than on a flat substrate.

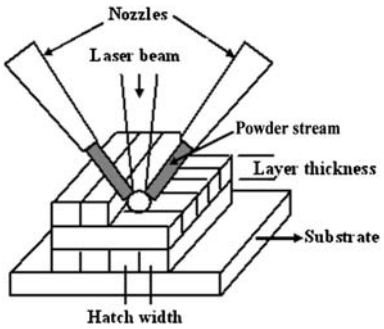

Fig. 1 Schematic of the LENS® process

While the LENS® process has successfully been applied to fabrication of engineering components in materials like stainless steels, tool steels, titanium alloys, and superalloys [10–14], there is little known about LENS® deposition of CoCrMo. In particular, the influence of the rapid thermal cycling involved in the process on the microstructure and properties of the resultant CoCrMo alloy is not well known. In view of the above, the current work was undertaken with the following objectives: (i) to examine the applicability of the LENS® process for fabricating dense, crack-free parts in CoCrMo; and (ii) to determine the influence of LENS® process parameters on CoCrMo microstructure, hardness and abrasive wear resistance. The ultimate goal of the project was to determine the applicability of LENS® deposited CoCrMo for use in implants with limited contact area, such as for knees.

Experimental work

The CoCrMo powder material used in the present work was obtained from Carpenter Technologies (Biodur CCM+, gas atomized, –100/+325 mesh size). Table 1 shows the chemical composition of the powder material. The substrates used were 5 mm thick disks cut from 55 mm diameter wrought bar stock of CoCrMo. Both the bar stock and the powder material alloy compositions conform to ASTM F 1537.

Deposits 50 mm long, 25 mm wide and 6 mm thick were produced using the Optomec 750 LENS® machine equipped with a 500 W Nd-YAG laser. The parameters employed for deposition are listed in Table 2. These parameters were found to result in crack-free deposits with minimum porosity and consistently higher hardness, and were arrived at after extensive preliminary deposition experiments involving the use of laser power, traverse speed, powder feed rate, layer thickness, and hatch spacing at various levels [15].

Sections cut from LENS® deposits were prepared following standard metallographic practices for microstructural examination. Microstructural studies were performed using an Axiovert 100A inverted light microscope and a Hitachi S 4000 Scanning Electron Microscope (SEM) equipped with a field emission gun. Polished

Table 1 Chemical composition of alloy CoCrMo powder/substrate (Biodur CCM+)

Element	Co	Cr	Mo	C	Mn	Si	Ni	Ti	Fe	S	P	N	O
Wt.%	61.78	29.37	6.52	0.23	0.69	0.68	0.05	0.01	0.11	0.002	0.003	0.18	0.01

Table 2 Parameters used for making the LENS® deposits

Parameter	Level
Laser power	285 W
Laser traverse speed	12.7 mm/s
Powder feed rate	0.57 g/min
Layer thickness	0.25 mm
Hatch spacing	0.38 mm

specimens were electrolytically etched with 5% HCl aqueous solution at 2 V for about 10 s. The volume fraction of carbide particles in the deposit microstructure was estimated using image analysis on SEM pictures.

Hardness tests were performed on transverse sections of the LENS® deposits using a Rockwell C hardness testing machine (minor load: 10 kg, major load: 140 kg). At least five tests were performed on each specimen and the average values were reported. Dry sand/rubber wheel abrasive wear tests were performed on LENS® deposits conforming to the requirements of ASTM G65-94 (Procedure A). Figure 2 shows a schematic of the wear test set-up. The wear tests were performed for 6,000 revolutions (wheel dimensions: 225 mm diameter, 12 mm width) at an applied force of 130 N using a sand flow rate of 300 g/min. Prior to testing, the specimen surface was milled and final polished with 320 grade sandpaper in the direction of wheel rotation. The amount of weight loss in test specimens after wear testing was taken as the measure of wear resistance. Microstructural, hardness and wear studies were also performed on CoCrMo unused wrought substrate material for comparison.

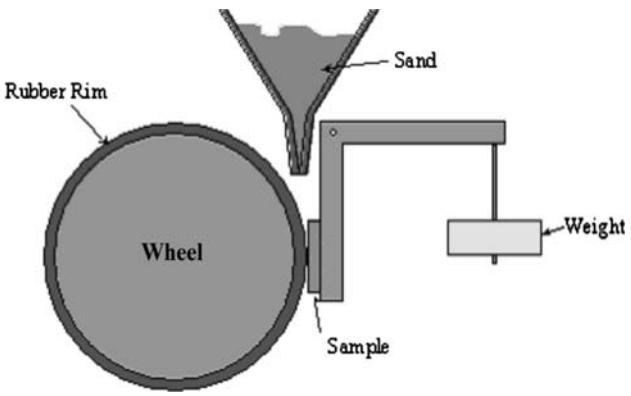

Fig. 2 Schematic of the dry sand/rubber wheel wear test set up

Results and discussion

Microstructures

The CoCrMo wrought substrate (transverse section) showed a very fine grain size (15–20 μm) with a number of regularly shaped carbide particles (particle size: 3–4 μm) uniformly distributed in the matrix (Fig. 3). The volume fraction of carbide particles in the wrought substrate material was found to be approximately 7 vol.%. These microstructural features are typical in CoCrMo wrought materials and the carbide particles present in CoCrMo are known to be predominantly $(Cr, Mo)_{23}C_6$ type, which are primarily responsible for the alloy's excellent wear resistance [9, 15]. The substrate material used in the present investigation was processed through a powder metallurgy + hot isostatic pressing route which, as contrasted with the conventional ingot metallurgy route, ensures fine grain size and uniform distribution of carbide particles without the chemical segregation effects in wrought products [9].

Figure 4 shows the optical microstructure of a CoCrMo LENS® deposit (transverse section). The deposit exhibited the characteristic layered microstructure with good bonding between individual tracks and layers without any porosity, cracks, or lack of fusion defects. The substrate/deposit interface was found to be sound with a narrow heat-affected zone (HAZ) (Fig. 5). Epitaxial growth features, typical in weld metal solidification, were observed at the substrate/deposit interface. Also, the carbide particles were found to be absent in the HAZ, as can be seen in Fig. 5. This indicates that the temperatures in the HAZ reach as high as 1,200°C (CoCrMo is generally solution treated at this temperature) when the first layer is deposited, resulting in dissolution of carbide particles. However, the HAZ is extremely thin (25–30 μm), as can be seen in Fig. 5, due to the very low and extremely localized heat inputs involved in the in the LENS® process.

Examination at higher magnification revealed varying solidification features in the LENS® deposit (Fig. 6). Generally, each layer consisted of a mixture of slightly coarser columnar dendrites (located at the bottom, marked "A" in Fig. 6a) and very fine equiaxed dendrites (located in the top portion, marked "B" in Fig. 6a). Similar microstructural variations were identified in various other LENS®-processed materials [11, 13, 14]. These variations in deposit microstructure arise from variations in local

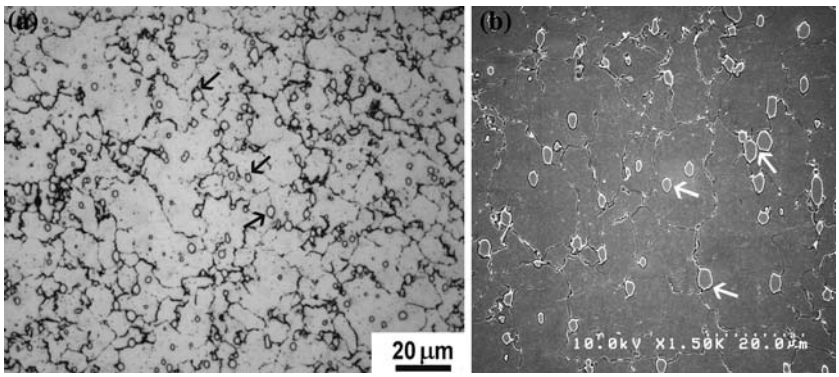

Fig. 3 Microstructures of the CoCrMo wrought substrate material: (**a**) Optical and (**b**) SEM. Arrows show carbide particles

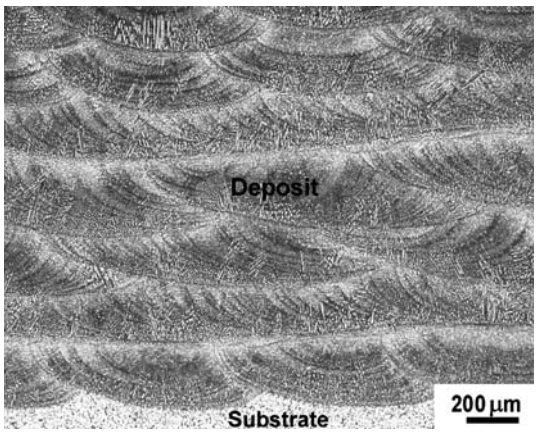

Fig. 4 Low magnification optical micrograph of the CoCrMo LENS® deposit (transverse section)

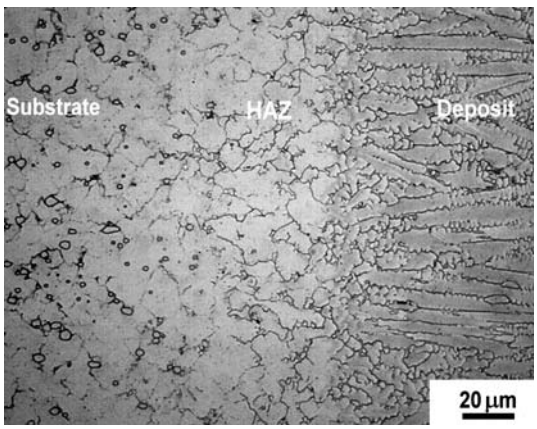

Fig. 5 Optical microstructure at the deposit/substrate interface showing epitaxial growth features and a thin heat-affected region (HAZ) with dissolved carbide particles

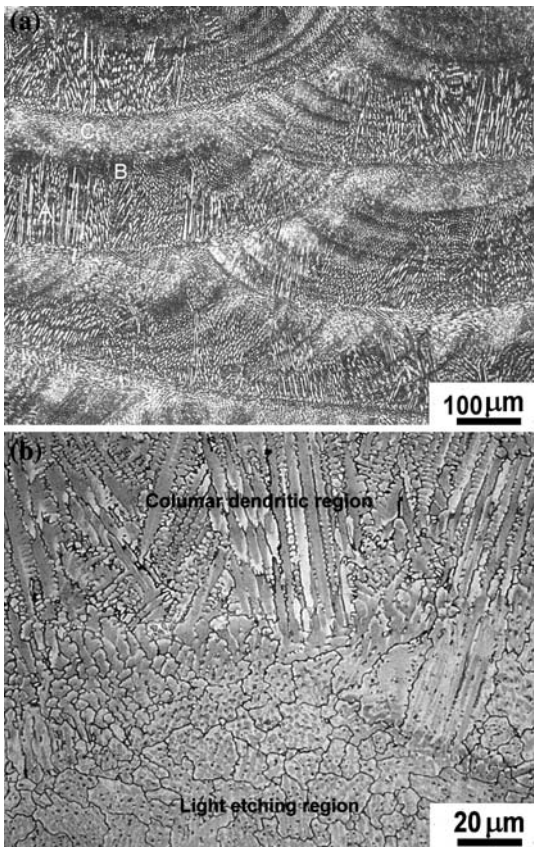

Fig. 6 Optical microstructures of the CoCrMo LENS® deposit: (**a**) Columnar dendritic (A), fine equiaxed dendritic (B) and light etching (C) regions in deposit microstructure; (**b**) light etching region at a higher magnification showing slightly coarser equiaxed dendrites/grains

solidification conditions. Further, in each layer a thin light etching region was found to occur just below the layer deposited above it (marked "C" in Fig. 6a). A high magnification picture of this light etching region is shown in Fig. 6b, which consisted of slightly coarser equiaxed dendrites/grains compared to those present in region "B". This light etching region is in essence a HAZ within previously deposited material due to newly deposited material, and is a result of the multiple thermal cycling effects associated with the LENS® process, as noted previously in laser deposited H13 tool steel [11]. Overall, the scale of the solidification structure can be seen to be very fine, reflecting the extremely high cooling rates (in the range of 10^4–10^5°C/s) associated with the LENS® process [16].

This is a significant advantage of LENS®, as the slow cooling rates associated with conventional casting techniques often result in coarse-grained structures.

SEM examination clearly revealed the carbide particles present in the deposit microstructure. Figures 7a and b show the carbide particles in the columnar dendritic and equiaxed dendritic regions present in the deposit microstructure. The upper portion of Fig. 7b corresponds to the light etching region noted in Fig. 6. The carbide phase in this region was observed to be present as a thin continuous network. The bottom portion of Fig. 7b corresponds to the fine equiaxed dendritic region in the deposit microstructure. The carbide particles can be seen to be present mainly in the interdendritic regions throughout the deposit microstructure indicating that they formed towards the latter stages of solidification. During solidification of alloy CoCrMo, C is rejected at the solid/liquid interface, which then accumulates in the interdendritic liquid. Solidification terminates with a eutectic-type reaction forming eutectic carbides in the interdendritic regions [17]. The average volume fraction of carbides in the deposit microstructure was found to be approximately 6.5 vol.%, which is comparable to that in the wrought substrate. Fig. 7c shows the carbide particles at a higher magnification (in the equiaxed dendritic region) clearly revealing the carbide morphology. The size, shape and distribution of carbides in the deposit microstructure were found to be significantly different from those in the wrought substrate microstructure. The carbide particles in the deposit microstructure can be seen to be very thin (less than 1 μm thick) and long, which is significantly different than the mostly spherical, uniformly distributed carbide particles in the substrate microstructure. Also, the carbide phase was found to occur as a continuous network at many locations in the deposit microstructure, as can be seen in Figs. 7a and b.

Hardness and wear resistance

The results of hardness and dry sand/rubber wheel wear tests are given in Tables 3 and 4, respectively. While the deposit hardness was found to be comparable with the wrought substrate hardness, interestingly, abrasive wear resistance of the deposit was found to be significantly lower than that of the wrought substrate. Wear resistance of

Table 3 Results of Rockwell C hardness tests (average of five measurements)

Specimen	Hardness (HRC)
LENS® deposit	40
Wrought substrate	41

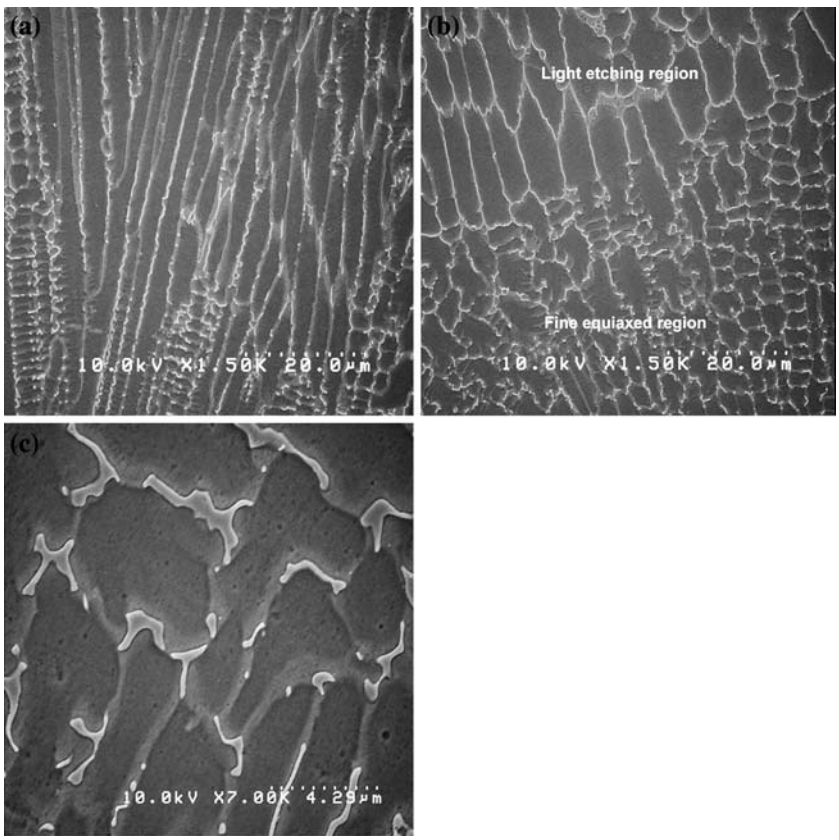

Fig. 7 SEM microstructures of the CoCrMo LENS® deposit showing interdendritic carbide particles: (**a**) Columnar dendritic region, (**b**) Fine equiaxed dendritic and light etching regions, and (**c**) Equiaxed dendritic region at a higher magnification

Table 4 Results of dry sand/rubber wheel abrasive wear tests (average of three specimens)

Material	Weight loss (g)
LENS® deposit	6.45
Wrought substrate	2.70

alloy CoCrMo is primarily governed by the amount and morphology of hard carbide particles present in the microstructure [8, 18]. The inferior wear resistance of the LENS® deposit is attributable to the presence of the carbide phase as irregularly shaped, very thin, long, interconnected particles, as a thin continuous network in the deposit microstructure. The carbide phase when present in the form of a continuous film or in the form of thin, long interconnected particles is easily removed during the dry sand/rubber wheel wear test conditions, offering less wear protection to the matrix. On the other hand, the optimum sized, regularly shaped and uniformly distributed carbide particles present in the substrate microstructure offer superior wear resistance. It is likely that this decrease in abrasive wear resistance is due simply to the fact that there was an order of magnitude decrease in the size of the carbide precipitates, and thus a commensurate reduction in its ability to resist the gouging abrasive wear mechanism present in the test.

The occurrence of the carbide phase in LENS® deposited CoCrMo as a continuous film-like morphology, or as a thin, long interconnected particle morphology might also adversely affect the tensile ductility and fatigue properties of the material, as the continuous nature of the carbides may lead to easier crack propagation. It is interesting to note that the above-noted morphological deficiencies in the carbide microstructure did not affect the deposit hardness.

The present study shows that use of the LENS® process for fabrication of prosthetic devices in CoCrMo has potential, but must be carefully studied further. While satisfactory deposits without any porosity or cracks can be made using the LENS® process, the process results in a carbide morphology that affects the abrasive wear resistance, and possibly other properties, of the material. It should be noted, however, that the problems encountered with LENS® deposits are similar to those encountered with investment casting of CoCrMo implants. In addition, it is critically necessary to evaluate LENS® deposit wear performance using like-on-like wear tests (such as a pin-on-disc sliding wear test as per ASTM G99), which more closely represent the actual service conditions of an implant in order to fully assess the suitability of the process for fabricating CoCrMo implant devices. However, the following strategies may be adopted in future work to improve the wear resistance of CoCrMo LENS® deposits: (i) post-deposition heat treatments to dissolve and reprecipitate the carbide particles for a more optimum size and morphology, (ii) an increase in carbon content to cause greater volume fractions of carbide particle precipitates, (iii) further optimization of the process parameters to avoid continuous carbide film formation.

Conclusions

Fully dense, metallurgically sound CoCrMo deposits have been demonstrated using the LENS® process. LENS® deposited CoCrMo exhibits extremely fine microstructures, with a comparable carbide volume fraction and hardness to CoCrMo wrought materials. LENS® deposited CoCrMo exhibits a carbide morphology with very thin, long interconnected carbide particles and continuous carbide networks leading to inferior abrasive wear resistance under dry sand/rubber wheel test conditions when compared to wrought CoCrMo material. The LENS® process is potentially suitable for fabrication of CoCrMo biomedical implant devices, but further work is required to determine the effects of the fine, continuous carbide morphology on like-on-like wear, fatigue life, and strength properties, and whether post-deposition heat treatments may improve these properties.

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