Functionally graded Co–Cr–Mo coating on Ti–6Al–4V alloy structures

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Abstract

Functionally graded, hard and wear-resistant Co–Cr–Mo alloy was coated on Ti–6Al–4V alloy with a metallurgically sound interface using Laser Engineering Net Shaping (LENS™). The addition of the Co–Cr–Mo alloy onto the surface of Ti–6Al–4V alloy significantly increased the surface hardness without any intermetallic phases in the transition region. A 100% Co–Cr–Mo transition from Ti–6Al–4V was difficult to produce due to cracking. However, using optimized LENS™ processing parameters, crack-free coatings containing up to 86% Co–Cr–Mo were deposited on Ti–6Al–4V alloy with excellent reproducibility. Human osteoblast cells were cultured to test in vitro biocompatibility of the coatings. Based on in vitro biocompatibility, increasing the Co–Cr–Mo concentration in the coating reduced the live cell numbers after 14 days of culture on the coating compared with base Ti–6Al–4V alloy. However, coated samples always showed better bone cell proliferation than 100% Co–Cr–Mo alloy. Producing near net shape components with graded compositions using LENS™ could potentially be a viable route for manufacturing unitized structures for metal-on-metal prosthetic devices to minimize the wear-induced osteolysis and aseptic loosening that are significant problems in current implant design.

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Keywords: Functionally graded materials; Laser processing; Laser engineered net shaping (LENS); Biocompatibility; Osteoblast

1. Introduction

Over 200,000 total hip replacements (THRs) are performed in the USA each year. Although the average life time of an implant is 7–12 years, around 10% of the implanted prosthesis requires revision within 10 years. A short implant life is a significant problem, especially for the growing number of younger patients, because of their active lifestyle. The worldwide population of people younger than 40 years of age who receive hip implants is expected to be 40 million by 2010 [1]. Similarly, by 2030 the population of this age group is expected to be 80 million [1], which is likely to create a need for implants which can last longer in vivo. Such a trend is common in other load-bearing devices as well.

Although ultrahigh-molecular-weight polyethylene (UHMWPE) liner used in traditional hip replacements is durable, the rate of wear is still significant and is a cause of serious concern due to osteolysis. Osteolysis and aseptic loosening have been identified as major factors limiting the life of prostheses, with indications that fine UHMWPE wear debris [2–6], generated primarily at the interface between the femoral head and the acetabular cup, promotes this degradation. Thus, wear-particle-induced bone loss is one of the main limiting factors affecting the long-term stability of UHMWPE liner-based THR and other load-bearing implants in which UHMWPE is used [7–9]. The hypothesis is that implant-derived wear particles, and other wear products, induce a foreign body inflammatory response in the joint capsule and along implant–bone interfaces, which results in bone loss and therefore aseptic loosening. Due to this concern, there is considerable interest in alternative wear-resistant systems. Such alternatives include ceramic-on-ceramic (CC) and metal-on-metal (MM) configurations.

Hip simulator testing has shown that an MM bearing has considerably less linear and volumetric wear than a
metal-on-UHMWPE couple [10]. More importantly, this improved wear, seen on hip simulators, has been borne out in clinical retrievals [11–14], where a 40 times lower linear wear rate and 200 times lower volumetric wear rate than conventional UHMWPE bearings were observed [11–14]. Typically, these long-surviving MM implants had highly polished surfaces with minimal scratches, had the expected low wear and caused minimal osteolysis [15,16]. These results confirm that MM implants are viable alternatives to metal-on-UHMWPE implants [17]. Among various metallic implant alloys, Co–Cr–Mo alloys are the only materials used for MM hip implants because of their remarkable wear and corrosion resistance [18–20]. These alloys are known to possess a certain self-healing capacity – the ability to polish out visible surface scratches with continued wear cycles rather than to experience a progressive deterioration of the surface topography, leading to accelerated wear [21]. This is a valuable property in light of the possibility of entrapment of third-body wear particles between the articulating surfaces during in vivo service.

The most widely used materials for THR components are shown in Table 1. Wear debris essentially originates from the femoral head–acetabular liner and acetabular liner–shell interfaces. Titanium alloys are preferred for stems and shells because of their bone-friendly nature and low elastic modulus. Similarly, the femoral heads and acetabular liners are made using Co–Cr–Mo alloy due to their excellent wear resistance. However, when Ti alloy acetabular shells are used in combination with Co–Cr–Mo alloy liners, the wear of the shell dominates over the wear of the liner. In such cases the methodologies used to improve the wear resistance of the Ti alloy shell are very important. Ceramic coatings have been proposed, in the past, as being wear-resistant and a metal ion release barrier for THR. These coatings were obtained using different vapor deposition techniques, such as physical vapor deposition, ion implantation, sputtering and the coatings consisted of diamond-like carbon [22,23] or nitrides [24,25]. These coatings have found little application in the field of THR due to their inherent brittleness and catastrophic fracture possibilities. While a wear-resistant alloy coating on metal substrates seems plausible [26,27], there is only one metallic alloy combination, i.e. Co–Cr–Mo and Ti–6Al–4V, suitable for surgical implant, which shows metallurgical incompatibility. Interaction between cobalt and titanium at high temperature can lead to the formation of various intermetallic compounds, such as Ti2Co, TiCo2 and TiCo3 [28]. Moreover, the mismatch in elastic moduli, thermal expansion coefficient and hardness between the two materials could lead to excessive residual stresses in the coatings and consequent delamination or cracking of the coating. One way to overcome these problems is the use of functionally graded coatings (FGCs). In a functionally graded coating, an intermediate layer with a gradual compositional variation is applied between the top wear-resistant coating and the substrate. This layer consists of several sections composed of two alloys in various ratios, i.e. with gradual changes in composition and microstructure, and, therefore, its properties. Compared with regular multi-component coatings, FGCs can effectively reduce the discontinuity of thermal expansion coefficient between the materials, and also minimize the residual stresses in the coatings.

In this work, we have demonstrated the fabrication of functionally graded Co–Cr–Mo-coated Ti–6Al–4V alloy implants using Laser Engineering Net Shaping (LENS™), which ensures a metallurgically sound interface between the two alloys and increases the surface hardness. Such gradient structures provide useful mechanical support for the wear-resistant exterior layers and minimize the likelihood of localized Hertzian failure during implant service. Our work focuses on processing, coating characterization and in vitro biocompatibility of these LENS™-processed functionally graded structures.

2. Materials and methods

Ti–6Al–4V alloy powder (Advanced Specialty Metals, Inc., Nashua, NH) with particle size between 50 and 150 μm and Co–Cr–Mo alloy powder (Stellite Coatings, Goshen, IN) with 50–100 μm particle size was used in this study. The nominal composition (wt. %) of the Ti alloy was 6.37 Al, 3.86 V, 0.17 Fe, 0.18 O, 0.026 C, balance Ti, and that of the Co–Cr–Mo alloy was 27 Cr, 5.2 Mo, 0.3 C, 1.2 Fe, 0.7 Mn, 2.8 Ni, 1.6 Si, balance Co. Gradient samples of 10 mm diameter were fabricated on a substrate of 3 mm thick rolled, commercially pure Ti plates using LENS™/750 (Optomec Inc. Albuquerque, NM) equipped with a 500W Nd:YAG laser and a double powder feeder system. The first hopper contained Ti–6Al–4V alloy powder and the second hopper contained Co–Cr–Mo alloy powder. Samples were fabricated in a glovebox containing argon atmosphere with O2 content less than 10 ppm to limit oxidation of alloys during processing. The LENS™ process uses a Nd:YAG laser, up to 2 kW power, focused onto a metal substrate to create a molten metal pool on the substrate. Metal powder is then injected into the metal pool, which melts and solidifies. The substrate is then scanned relative to the deposition head to write a metal line with a finite width and thickness. Rastering of the part back and forth to create a pattern and fill material in the desired area allows a layer of material to be deposited. Finally, this procedure is repeated many times along the Z-direction, i.e. height, until the entire object represented

Table 1

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Femoral stems</td>
<td>Co–Cr–Mo alloy or titanium alloy</td>
</tr>
<tr>
<td>Femoral heads</td>
<td>Co–Cr–Mo alloy</td>
</tr>
<tr>
<td>Acetabular shells</td>
<td>Titanium alloy or Co–Cr–Mo</td>
</tr>
<tr>
<td>Acetabular liners</td>
<td>Polyethylene (UHMWPE) or cast Co–Cr–Mo alloy</td>
</tr>
</tbody>
</table>
in the three-dimensional CAD model is produced on the substrate.

Initially, a 5 mm thick Ti–6Al–4V alloy cylinder was made and four layers of Co–Cr–Mo alloy were deposited on top of this cylinder at various laser parameters without composition gradient across the two alloys. All of these coatings delaminated from the Ti alloy cylinder due to thermal stresses arise from the contraction during melting/re-solidification of Co–Cr–Mo alloy and their metallurgical incompatibility. Therefore, a gradient coating with gradual transition in composition from 100% Ti–6Al–4V alloy at the bottom to 100% Co–Cr–Mo alloy at the top is attempted to reduce the failure and to attain better interfacial bonding. These structures also showed radial cracks or delamination near the top portion of the transition region, indicating metallurgical incompatibility in the region with nearly 100% concentration of Co–Cr–Mo alloy. To further reduce the cracks/delamination and to identify the optimum concentration of Co–Cr–Mo alloy in the transition region, a few gradient structures with varying Co–Cr–Mo alloy concentrations were made. Gradient structures with 25%, 50%, 70% and 86% Co–Cr–Mo alloy on the top surface were made at 450 W laser power and 22.5 mm s⁻¹ scan speed. These compositionally graded structures consisted of 100% Ti–6Al–4V alloy in the first six layers. The composition in the transition region of the gradient structure was varied from 100% Ti–6Al–4V alloy at the first layer to various concentrations of Co–Cr–Mo alloy at the top layer over 5–6 layers. It has been shown that the use of LENS®-processed porous metals achieve stable long-term fixation due to bone cell ingrowth through open porosity [29]. Open porosity on one side of the structure can improve cell–material interactions [29,30], and hard coating on the other side increases the wear resistance of the structure. Therefore, in this work the first six layers of Ti–6Al–4V alloy were made at 200 W to create 30 vol.% porosity [29,30] and remaining layers were made at 450 W to reduce the porosity near the transition region. In the transition zone the powder feed rate for Co–Cr–Mo alloy increased from 0 to 46.5 g min⁻¹ over the number of transition layers. For Ti–6Al–4V alloy, it was 17.5 g min⁻¹ to start with and reduced to 0 g min⁻¹ over the same number of layers.

Microstructures of the samples were examined using both optical and scanning electron microscopy (SEM). The elemental distribution across the gradient structures and the composition of top surface was recorded using a field emission SEM (FEI-SIRION) equipped with a “Genesis EDAX” energy-dispersive spectrometer (EDS). Constituent phases in the top layer of the gradient samples were identified using a Siemens D 500 Kristalloflex diffractometer with Cu Kα radiation and compared with that of as-received powders. In order to track the compositional gradient across the deposit, a series of microhardness indentations were placed from one end of the deposit to the other end, with neighboring indents being separated by 0.2 mm using a Vickers microhardness tester (Leco, M-400G3) at 200 g load applied for 15 s.

All samples for cell culture test were sterilized by autoclaving at 121 °C for 20 min. In this study the cells used were an immortalized, cloned osteoblastic precursor cell line 1 (OPC1), which was derived from human fetal bone tissue [31]. OPC1 cells were seeded onto the samples placed in 24-well plates. Initial cell density was 5.0 × 10⁴ cells well⁻¹. A 1 ml aliquot of McCoy’s 5A medium (enriched with 5% fetal bovine serum and 5% bovine calf serum, and supplemented with 4 µg ml⁻¹ of L-glutamine) was added to each well. Cultures were maintained at 37 °C under an atmosphere of 5% CO₂. Medium was changed every 2–3 days for the duration of the experiment.

The MTT (Sigma, St. Louis, MO) solution of 5 mg ml⁻¹ was prepared by dissolving MTT in PBS, and filter sterilized. The MTT was diluted (50 µl into 450 µl) in serum-free, phenol red-free Dulbeco’s minimum essential medium. Then 500 µl of diluted MTT solution was added to each sample in 24-well plates. After 2 h of incubation, 500 µl of solubilization solution made up of 10% Triton X-100, 0.1 N HCl and isopropanol was added to dissolve the formazan crystals. Then 100 µl of the resulting supernatant was transferred into a 96-well plate, and read by a plate reader at 570 nm. Data are presented as mean ± standard deviation. Statistical analysis was performed using Student’s t-test, and p < 0.05 was considered statistically significant.

All samples for SEM observation were fixed with 2% paraformaldehyde/2% glutaeraldehyde in 0.1 M cacodylate buffer overnight at 4 °C. Post-fixation was performed with 2% osmium tetroxide (OsO₄) for 2 h at room temperature. The fixed samples were then dehydrated in an ethanol series (30%, 50%, 70%, 95% and 100%, three times), followed by drying with hexamethyldisilane. After gold coating, the samples were observed under SEM for cell morphologies.

3. Results

3.1. Microstructures and phase analysis

Laser processing resulted in fine grained microstructures in all the samples. Fig. 1 shows cross-sectional microstructures of graded Co–Cr–Mo alloy coating on Ti–6Al–4V alloy. The graded structures exhibited good bonding between individual layers without any gross porosity, cracks or lack of fusion defects. However, unmelted or partially melted Ti–6Al–4V alloy powder was observed especially in the first layer of transition region and at the interface between individual layers. Relatively less unmelted Ti–6Al–4V alloy powder was observed at the interface between the individual layers than in the first layer of transition region. Moreover, the amount of unmelted powder gradually decreased towards the top surface of the coating, i.e. with increasing Co–Cr–Mo content.
Top surface microstructural variation as a function of Co–Cr–Mo alloy concentration of graded structures is shown in Fig. 2. As the Co–Cr–Mo alloy content increased, the most significant change in the micrographs was the decrease in the volume fraction of the Ti–6Al–4V alloy phase (the phase with the darker contrast in the micrographs) and the consequent increase in the volume fraction of Co–Cr–Mo alloy (the phase with the lighter contrast). Notable change was also observed in the morphology and scale of the Co–Cr–Mo alloy phase as the amount was increased. As shown in Fig. 2a, for 25% Co–Cr–Mo alloy content, the phase/precipitates were thin and continuous predominantly along Ti–6Al–4V alloy grain boundaries. However, as the Co–Cr–Mo alloy content increased, a bimodal size distribution of precipitates formed in the microstructure with large chunks of precipitates (Fig. 2b). Fig. 2c shows that at 70% Co–Cr–Mo concentration the grain boundary precipitation/phase was completely replaced by a two-phase microstructure.

Fig. 3 presents the XRD results of as-received alloy powders and laser-processed gradient structures. All the peaks from the top surface of the gradient structures correspond to as-received Ti–6Al–4V or Co–Cr–Mo powders without any intermetallic compounds. These results at various Co–Cr–Mo alloy concentrations also indicate the absence of intermetallics throughout the transition region of these gradient structures. Table 2 shows the top surface composition of compositionally graded structures with various Co–Cr–Mo alloy concentrations on top. The composition along the gradient region was measured using EDS in the SEM, and a typical Co concentration gradient in the transition region of graded alloy structures is shown in Fig. 4. The gradual increase in the Co concentration from Ti–6Al–4V alloy substrate towards the top coating is clear. In order to track the compositional gradient across the deposit systematically, a series of microhardness indent markers were placed from one end of the transition region to the other. The hardness increased gradually with increasing Co–Cr–Mo concentration, as shown in Fig. 5. The average top surface hardness also increased with increasing Co–Cr–Mo alloy concentration, as shown in Table 2. The hardness of the top surface increased from 588 ± 27 to 947 ± 22 HV when the Co–Cr–Mo alloy concentration at the top surface was increased from 25 to 86% in the coating. These hardness values are significantly higher than the average hardness of the laser-deposited Ti–6Al–4V alloy, which was 333 ± 16 HV.

3.2. In vitro biocompatibility

Fig. 6 shows the morphology of OPC1 cells on graded Co–Cr–Mo coatings deposited on Ti–6Al–4V alloy samples after 14 days of culture. Cells on laser-processed 100% Ti–6Al–4V alloy samples had a flattened morphology with numerous filopodia extensions covering almost the entire surface. In contrast, fewer cells were observed on the laser-processed 100% Co–Cr–Mo alloy sample, and these exhibited an elongated morphology with only a few
filopodia extensions. The cell morphology of graded structures with varying concentrations of Co–Cr–Mo alloy in the top coating was similar to that observed on 100% Ti–6Al–4V alloy samples, which spread and grew well on the surface of these samples. The amount of cells on the samples as determined by MTT assay is shown in Fig. 7. Statistical analysis was performed on MTT data using Student’s t-test, and \( p < 0.05 \) was considered statistically significant. Maximum cell density was observed on the 100% Ti–6Al–4V alloy sample. The cell density on the 100% Co–Cr–Mo alloy sample was relatively low, at only one-quarter of those on 100% Ti–6Al–4V alloy sample. The cell numbers on the graded structures decreased gradually with increasing Co–Cr–Mo alloy concentration in the top surface. Nevertheless, the cell density on these graded structures was higher than those observed on the 100% Co–Cr–Mo alloy. These in vitro results confirm that all the samples were non-toxic and biocompatible.

4. Discussion

Alloy or elemental blends can be used to prepare complex alloys that are chemically and microstructurally identical to alloys prepared from pre-alloyed powders using LENS™. However, in alloy/elemental blends the laser absorption coefficient, melting point, concentration and enthalpy of mixing of alloy/elements all have a significant effect on the laser energy required for chemical homogeneity [32]. It is shown that the use of elemental blends requires significantly greater energy than the use of pre-alloyed...
powders of the same alloy [32]. In this work, the composition gradient in the transition region containing 5–6 layers is achieved by controlling the feed rate of two powder feeders one filled with Ti–6Al–4V alloy powder and another with Co–Cr–Mo alloy powder. The lack of adequate intermixing in the first 2–3 layers of the transition region deposited under similar conditions appears to be a direct consequence of the effect of temperature fluctuations in the liquid metal pool due to changes in the composition. When the deposition process changes from the 100% Ti–6Al–4V alloy layer to a mixture of the two alloys, in the first layer of the transition region, the Co–Cr–Mo alloy, having a lower melting point (1260–1265 °C) than the Ti–6Al–4V alloy (1604–1660 °C), melts immediately by absorbing heat from the liquid metal pool, thereby decreasing the temperature of the melt pool. In addition, the finer powder size of the Co–Cr–Mo alloy (50–100 μm) than the Ti–6Al–4V alloy (50–150 μm) also aids the easier and earlier melting of the Co–Cr–Mo alloy. Because of the lower liquid metal pool temperatures in the first layer of the transition region, some of the large Ti–6Al–4V alloy powders did not melt completely. As the deposition process proceeds with subsequent layers with increasing Co–Cr–Mo concentration, the amount of unmelted powder decreases

Table 2
Composition and hardness of top surface in functionally graded Co–Cr–Mo coatings on Ti–6Al–4V alloy structures

<table>
<thead>
<tr>
<th>Element</th>
<th>25% Co alloy</th>
<th>50% Co alloy</th>
<th>70% Co alloy</th>
<th>86% Co alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>63.20</td>
<td>42.32</td>
<td>24.19</td>
<td>8.17</td>
</tr>
<tr>
<td>Al</td>
<td>5.79</td>
<td>3.29</td>
<td>3.58</td>
<td>4.22</td>
</tr>
<tr>
<td>V</td>
<td>3.64</td>
<td>2.35</td>
<td>2.75</td>
<td>1.74</td>
</tr>
<tr>
<td>Co</td>
<td>20.70</td>
<td>35.33</td>
<td>45.29</td>
<td>54.87</td>
</tr>
<tr>
<td>Cr</td>
<td>5.60</td>
<td>14.79</td>
<td>20.67</td>
<td>26.14</td>
</tr>
<tr>
<td>Mo</td>
<td>1.07</td>
<td>1.92</td>
<td>3.52</td>
<td>4.86</td>
</tr>
<tr>
<td>Hardness</td>
<td>588 ± 27</td>
<td>670 ± 28</td>
<td>789 ± 38</td>
<td>947 ± 22</td>
</tr>
</tbody>
</table>

Fig. 3. XRD pattern of as-received powders and top surface of gradient coatings.

Fig. 4. Typical Co distribution across the graded Co–Cr–Mo coatings on Ti–6Al–4V alloy.
due to the decrease in the amount of Ti–6Al–4V alloy powder fed into the liquid metal pool. Moreover, with increasing Co–Cr–Mo concentration, the melt pool temperature increases gradually due to the additional heat provided by the exothermic mixing between titanium and cobalt. The enthalpy of mixing Co with Ti increases from –22.27 to –37.58 kJ mol\(^{-1}\) as the fraction of Co in the mixture is increased from 0.21 to 0.55 [33]. The increasing additional heat supplied by this exothermic mixing compensates for any drop in melt pool temperature as the Co–Cr–Mo concentration increases. This explains the disappearance of unmelted Ti–6Al–4V powder in the top layer of the transition region. A similar effect of enthalpy of mixing on the homogeneity of LENS\textsuperscript{TM}-deposited Ti alloys using elemental powder blends has also been reported [34]. The unmelted powder can be eliminated either by increasing the laser energy input or by using a finer alloy powder.

A decrease in the volume fraction of the Ti–6Al–4V alloy phase in the top surface microstructure with increasing Co–Cr–Mo alloy concentration is understandable. The presence of Co–Cr–Mo alloy as a thin and continuous phase along the Ti alloy grain boundaries in low Co–Cr–Mo alloy samples indicates that this phase solidified towards the latter stages of solidification. As the Co–Cr–Mo alloy increases, the size and morphology of the Co–Cr–Mo alloy phase changes due to its higher volume fraction in the molten alloy pool. A gradual increase in the cobalt concentration from the Ti alloy substrate towards the top coating validates the potential of the LENS\textsuperscript{TM} process in creating unique microstructural gradients across the compositionally graded surfaces/coatings, which are difficult to process using traditional manufacturing routes.

In metal-on-metal implants, wear is a combination of adhesive and abrasive mechanisms. Fatigue wear is also possible in which repetitive loading of localized regions causes surface and subsurface cracks to propagate, producing wear debris. Under such conditions, wear resistance of any alloy is primarily governed by microstructural features, such as the amount, morphology and distribution of hard particles in the matrix. For example, wrought Co–Cr–Mo alloy possesses superior wear performance because of the small, finely distributed carbides in the microstructure rather than the coarse, continuous or more widely spaced carbides in the cast alloy [35–38]. Moreover, the grain size of wrought alloy is usually below 10 \(\mu\)m, whereas it is between 30 and 1000 \(\mu\)m for cast alloys. This huge difference in grain size significantly increases the strength of wrought alloy and also the wear-resistance [36,39]. The overall scale of the solidification structure of our graded coatings is very fine, reflecting the extremely high cooling rates (in the range of \(10^3–10^5\) K s\(^{-1}\)) associated with the LENS\textsuperscript{TM} process. This is a significant advantage of LENS\textsuperscript{TM}, as the slow cooling rates associated with conventional casting techniques often result in coarse-grained structures with the formation of various intermediate phases and associated poor wear resistance. Titanium and cobalt are metallurgically incompatible [28], and their interaction at high temperature could lead to intermetallic compounds such as Ti\(_2\)Co, TiCo\(_2\), and TiCo\(_3\). However, our laser-processed gradient structures did not show any intermetallic compounds in the transition region or on the top surface. This is due to the rapid cooling rates associated with laser processing, which limits the interaction time between the Ti and Co at high temperatures. Elimination of intermetallic compounds is beneficial in terms of better wear and biocompatibility of these graded structures. Gradient coatings with 86% Co–Cr–Mo in the top surface showed an ~184% increase in surface hardness. The finer grain size, uniform microstructure and high hardness of this laser-processed gradient coating can provide better wear resistance compared with conventionally cast alloy of this type [36,39]. Moreover, the porosity on the Ti–6Al–4V alloy side, which will be in contact with bone, can improve cell–material interactions [29,30], and the hard coating on the other side increases the wear resistance of the structure in contact with Co–Cr–Mo femoral heads.

Ti–6Al–4V and Co–Cr–Mo alloys are widely used biomedical alloys because of their excellent biocompatibility.
However, graded coatings with varying concentrations of Co–Cr–Mo alloy on Ti–6Al–4V alloy contain different microstructural constituents in the top surface. In vitro biocompatibility tests will evaluate the possible toxic effect of new microstructural constituents that are formed in these graded coatings. Cell attachment is the most critical stage of cell–materials interactions. Cells attach to the surface of materials via filopodia and lamellipodia [40]. Cells use these structures for attachment and migration. In this work, cell morphology and density changed due to the application of gradient Co–Cr–Mo alloy coating onto Ti–6Al–4V alloy. Cell morphology changed from numerous filopodia extensions in 100% Ti–6Al–4V alloy to very few extensions for 100% Co–Cr–Mo alloy. For gradient samples, as a first approximation, the cell–materials interactions and hence the biocompatibility can be assumed to be proportional to the relative concentrations of the two alloys in the coating surface. Being a more biocompatible alloy, a higher concentration of Ti–6Al–4V alloy in the coating surface would result in enhanced biocompatibility. Therefore, coatings with a high concentration of Ti–6Al–4V are more likely to exhibit better cell–materials interactions. This prediction has been confirmed by MTT assay, which shows a higher living cell density on the coating surface with increasing Ti–6Al–4V concentration. The cell density on graded coatings increased with decreasing concentration of the Co–Cr–Mo alloy, approaching the cell density observed on 100% Ti–6Al–4V alloy. The cell density on gradient coatings with 86% Co–Cr–Mo in the top surface is more than double that observed on 100%
Co–Cr–Mo alloy. A further increase in cell density is seen with decreasing Co–Cr–Mo alloy concentration down to 25% in the graded coatings. These results indicate that graded Co–Cr–Mo coatings on Ti–6Al–4V alloy with fine and uniform microstructure having high hardness and biocompatibility can be produced using LENS™. Moreover, the unique advantage of using LENS™ is its ability to fabricate such hard and wear-resistant graded coatings with or without porosity on one side of the structure to improve the cell ingrowth into these structures. Surface hardness increased from 333 to 947 HV with increasing Co–Cr–Mo concentration in the top surface of graded coatings. All the coatings are non-toxic and showed more than double the living cell density on the coating surface than 100% Co–Cr–Mo alloy surface. Our results indicate that a 50% Co–Cr–Mo alloy surface provides the best combination of wear resistance and biocompatibility.

5. Conclusions

Using the LENS™ process, deposition of hard and wear-resistant Co–Cr–Mo alloy graded coatings on Ti–6Al–4V alloy has been successfully demonstrated. Moreover, the inherent advantage of this process is its ability to fabricate graded structures with or without porosity on one side of the structure to improve the cell ingrowth into these structures. Surface hardness increased from 333 to 947 HV with increasing Co–Cr–Mo concentration in the top surface of graded coatings. All the coatings are non-toxic and showed more than double the living cell density on the coating surface than 100% Co–Cr–Mo alloy surface. Our results indicate that a 50% Co–Cr–Mo alloy surface provides the best combination of wear resistance and biocompatibility.

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