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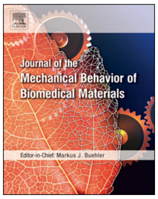

In situ reactive multi-material Ti6Al4V-calcium phosphate-nitride coatings for bio-tribological applications

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ABSTRACT

To reduce the wear related damage of medical grade Ti-6Al-4V alloy, laser engineered net shaping (LENS™) based *in situ* reactive multi-material additive manufacturing was employed to process a mixed coating of Ti-6Al-4V powder and calcium phosphate (CaP) in an oxygen free, nitrogen-argon environment. The resultant coatings were composite materials of titanium nitrides and calcium titanate in an α-Ti matrix. Hardness was increased by up to ~148% to 868 ± 9 HV as compared to the untreated Ti-6Al-4V substrate. Similarly, when tribological properties were evaluated in deionized (DI) water medium against alumina counter material, the wear damage was reduced by ~91% as compared to the untreated Ti-6Al-4V substrate. Furthermore, the untreated Ti-6Al-4V substrate released Ti ions of ~12.45 ppm concentration during wear whereas the Ti6Al4V-5%CaP coating processed in an argon-nitrogen environment released ions of ~3.17 ppm concentration under similar testing conditions. The overall coefficient of friction was also found to decrease due to the addition of CaP and processing the Ti6Al4V-CaP mixture in an argon-nitrogen environment. Our results indicate that this reactive multi-material additive manufacturing of metal-ceramic composites is an effective way of enhancing the tribological performance of metallic materials.

1. Introduction

Titanium and its alloys are one of the most sought after engineering materials. These metallic materials such as the Ti-6Al-4V alloy are characterized by high modulus, low density, and excellent resistance to corrosion as well as high temperature stability (Bandyopadhyay et al., 2016). For many applications, good resistance to wear and surface degradation for these metallic materials is also desired. From specifically a biomedical point of view, Ti based implant materials are greatly desired since they have good bio compatibility and low density (Materials and Devices for Bone Disorders et al., 2016; Balla et al., 2007). In load bearing implants, Ti based metallic materials are often used in configurations where they are in contact with other metallic, ceramic, or polymeric surfaces. The metallic surfaces could be other Ti surfaces, ceramic surfaces could be materials such as aluminum oxide (alumina) or zirconium oxide (zirconia), and polymeric surfaces could be ultra-high molecular weight polyethylene (UHMWPE) (Rahaman et al., 2007; Amstutz and Le Duff, 2006). In any of these configurations, the Ti based materials undergo wear (Miller and Holladay, 1958; Davidson et al., 1993; Khan et al., 1996). Wear of metallic surfaces leads to the creation of metallic particles that are then released into the human biological system. These metal particles can accumulate at implant sites, resulting in conditions such as metallosis and osteolysis. Implant surfaces that are manufactured to dimensional perfection could eventually lose their dimensional integrity from this wear, leading to sometimes catastrophic aseptic loosening of the implant (Ingham and Fisher, 2000; Archibeck et al., 2000; Black et al., 1990; Goldring et al., 1993). The direct and indirect issues arising out of wear of the surfaces in contact are further exacerbated due to the corrosive nature of the physiological environment.

To counter these issues related to wear and surface damage, two main approaches are followed. The first approach involves using a "cushion" between two surfaces in contact. This concept is materialized by using polymeric lining of a material such as UHMWPE between two metallic implant surfaces. The aim in this approach is to avoid contact between the two erosive surfaces at the expense of a softer material. However, in the course of time, these "soft cushion" materials tend to wear and create wear debris. Thus, the problem of wear of surface is delayed, but not necessarily reduced, in the long term (Gunther and Rose, 1993; Kurtz et al., 2003). In the second approach, the metallic implant surfaces that are in contact are separated with a hard ceramic or metallic material. In this way, the relatively softer implant surfaces do not contact each other and are less likely to wear. Instead, the hard, ceramic materials come in contact with ceramic surfaces that improve

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the wear resistance by improving the surface hardness. In this category, metallic Ti implant surfaces are often separated by ceramics such as alumina or zirconia. In other configurations of the same concept, the implant surfaces themselves are coated with hard materials such as titanium nitride or diamond-like carbon. These techniques have proven to reduce wear in metallic implant surfaces by a fair extent (Pappas et al., 1995; Sonntag et al., 2012). Such ceramic materials are processed using established techniques such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods (Paschoal et al., 2003; Zhu et al., 2012), plasma and ion beam methods (Nolan et al., 2006; Knapp et al., 1996), conventional gas nitriding, and laser based gas nitriding (Man et al., 2006; Sahasrabudhe et al., 2016). These methods are effective in creating ceramic layers but suffer from certain drawbacks such as inability to process complex surfaces and shapes (for PVD, CVD and plasma methods) and heating effects in the substrate material (for plasma methods). Powder additive manufacturing methods such as LENS™ could help in reducing the problems associated with the processing of ceramic materials. LENS™ based additive manufacturing has been utilized for 3D fabrication of near net shaped components and coatings from different metallic and metal-ceramic composite systems (Bose et al., 2018; Bandyopadhyay et al., 2009; Balla et al., 2009, 2012, 2010; Zhang et al., 2015). A combination of the two aforementioned approaches for controlling wear damage and the benefits of direct additive manufacturing could be the key for reducing wear related damage in biomedical implants.

Titanium nitride ceramic based materials have been a viable candidate for biomedical implant applications where advanced tribological properties, better than what metallic materials offer, are desired. Many researchers have previously demonstrated the processing and tribological evaluation of titanium nitride through a variety of different techniques. Additive manufacturing techniques have also been successful in processing titanium nitride. Balla et al. demonstrated the direct processing of a mixture of TiN and Ti6Al4V alloy (Balla et al., 2012). Sahasrabudhe et al. demonstrated the combination of classical laser gas nitriding in a modern setup of LENS™ *in situ (*Sahasrabudhe et al., 2016*). In situ* reactive multi-material LENS™ processing of Ti-Si-Nitride coatings was demonstrated by Zhang et al. (2015). From these demonstrations, the usability of the LENS™ system for the processing of ceramics as well as the viability of metal-ceramic composites for tribological applications was proven. In the current research, attempt was made to process a mixture of Ti6Al4V alloy and calcium phosphate in an argon-nitrogen environment using a LENS™ system. This *in situ* reactive and multi-material approach of additive manufacturing resulted a composite structure of titanium nitrides, calcium phosphate, and calcium titanate in an alpha and beta titanium matrix.

In this non-conventional processing method, two or more materials are processed in a controlled reactive environment. Composites of biomedical grade CoCrMo alloy with calcium phosphate in the form of tricalcium phosphate was also reported to have improved tribological properties (Sahasrabudhe et al., 2018). Processing a mixture of Ti6Al4V and calcium phosphate is expected to yield a composite material of nitrides of titanium with calcium phosphate. The nitride ceramic rich phase could act as the hard surface to resist wear. On the other hand, the softer calcium phosphate addition is expected to lower the wear by undergoing preferential wear and also by possibly forming a surface lubricating film *in situ*. The materials are processed using LENS™ system and characterized using scanning electron microscopy (SEM) and x-ray diffraction (XRD) techniques. The evaluation of tribological performance was done by wear testing in DI water medium and analyzing the wear media for Ti ion leaching. Microhardness testing was also performed on the LENS™ processed metal-ceramic composites.

2. Experimental

2.1. Laser Engineered Net Shaping (LENS™)

LENS™ is a powder based, directed energy deposition based additive manufacturing technique (ASTM Standard F2792-12a, 2012). The LENS™ system allows us to process net shaped metallic or metal-ceramic components from computer aided design (CAD) files. The LENS™ system utilizes laser energy from a focused, 500 W continuous wave focused Nd:YAG laser beam with a wavelength of 1064 nm. This laser energy is used to melt the powder or mixtures of powders (metallic or ceramic) that are carried in a pressurized argon gas feed system into the focal point of the laser beam. The powder feed at the focal point of the laser meets on a stage upon which the powder melts from the laser energy and rapidly solidifies. The stage is capable of operating in a raster scanning fashion in X and Y directions. The CAD design controls the raster scanning motion and one line of material can be deposited at a time. By continued raster scanning according to the CAD design, successive lines can be deposited and eventually a layer is formed. Once a layer is deposited, the feed assembly (focusing laser and powder feeding nozzles) moves up in the Z direction by a distance defined by the CAD design. On top of the previously deposited layer, another layer can be deposited in similar raster scanning fashion. In this layer wise deposition, a complete three dimensional part can be formed. The LENS™ system comprises of a glove box inside which the build sequence occurs. This glove box is purged with argon, while the oxygen level is maintained below 10 ppm throughout the material processing time. The system has two powder feeders, or hoppers, which can be operated simultaneously. By doing so, alloying can be achieved during deposition. Compositionally graded structures can be formed by using the two powder feeders in the same design but at different times. In addition to alloying and compositionally graded structures, LENS™ can also be used to form thermally graded structures. This can be achieved by altering processing parameters such as laser power, scan speed, and the powder feed rate (Bontha et al., 2006; Collins et al., 2003).

2.2. *In situ fabrication of nitride-CaP composite coating on titanium*

Laser processing of Ti6Al4V-CaP composites was done using premixed powder mixtures of Ti-6Al-4V alloy (ATI Powder Metals, 99.99% Purity and powder size between 45 and 149 μm) and Hydroxyapatite powder (Berkeley Advanced Biomaterials Inc., 99.99% purity and average particle size of 500 nm). A Ti-6Al-4V alloy plate (3 mm thick and 99.99% pure, President Titanium, Hanson, MA USA) was used as the substrate material for LENS™ deposition. Premixed powders were made by mixing Ti6Al4V powder with 2 wt% and 5 wt% of CaP in Ti6Al4V powder. Powder mixtures were then ball milled for 30 min to homogenize the mixture. These premixed powders were processed using LENS™ system described above. For *in situ* reactive additive manufacturing, the LENS™ system was first purged with argon and the oxygen level was reduced to less than 10 ppm. Once the low level of oxygen was achieved, nitrogen gas was purged for 10 min at a pressure of 35 psi. Samples were processed in this controlled chamber after nitrogen purging and during the entire processing time the oxygen level was continuously monitored and kept below 10 ppm. Square-shaped samples with 14 mm sides were fabricated at a constant laser power of 400 W and a raster scan speed of ~80 cm/min. One ~1.25 mm layer of designed layer thickness was deposited for each composition of the premixed powders on the Ti-6Al-4V substrate.

2.3. Characterization of Ti6Al4V-CaP-nitride coatings

The Ti6Al4V-CaP nitride coatings were cut using a low speed diamond saw (MTI Corporation) to facilitate the cross-sectional microstructure examination. Cut cross sections were mounted and then ground and polished to a mirror finish. Grinding was done using SiC