Materials and Design 109 (2016) 98–111

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

A new approach to develop palladium-modified Ti-based alloys for biomedical applications

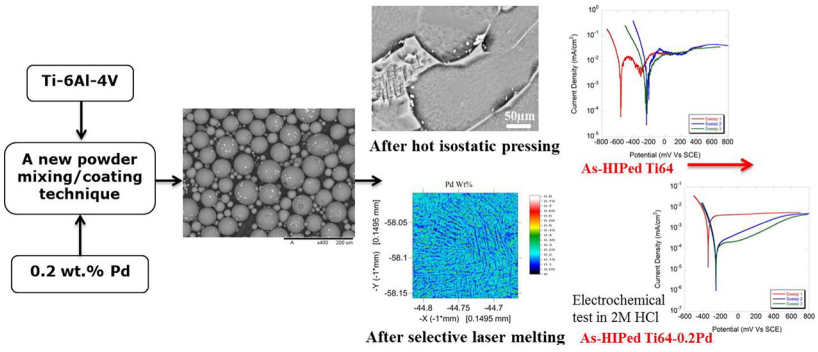
Chunlei Qiu [a,c,*], Andrew Fones [b], Hugh G.C. Hamilton [b], Nicholas J.E. Adkins [c], Moataz M. Attallah [c]

[a] School of Engineering, Cardiff University, The Parade, Cardiff CF24 3AA, UK
[b] Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common, Reading RG4 9NH, UK
[c] School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

HIGHLIGHTS

- Pd was evenly distributed among Ti-6Al-4V particles using a new mixing technique.
- Pd has dissolved completely into Ti-6Al-4V matrix after selective laser melting.
- With the addition of Pd, the corrosion resistance of the Ti alloy has been improved.
- Coarser grain structure also improves corrosion resistance of the Ti alloy in 2 M HCl.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 April 2016
Received in revised form 20 June 2016
Accepted 12 July 2016
Available online 14 July 2016

Keywords:
Selective laser melting
Hot isostatic pressing
Ti-6Al-4V
Microstructure
Corrosion behaviour
Tensile behaviour

ABSTRACT

A new powder mixing/coating technique combined with selective laser melting (SLM) or hot isostatic pressing has been used to modify Ti-6Al-4V (Ti64) with Pd with the aim of further improving its corrosion resistance. The modified alloy samples were characterised in terms of porosity, surface structure, microstructure and composition using optical microscopy (OM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and electron microprobe analysis (EPMA). Their corrosion properties were evaluated via electrochemical tests and the mechanical properties measured via tensile tests. Using a new physical powder mixing technique, Pd was homogeneously distributed among the base Ti alloy powder particles without damaging their sphericity. After HIPing Pd is mainly located at grain boundaries while during SLM Pd has dissolved into the matrix. The porosity in the as-SLMed samples and surface roughness both increase continuously with increased laser scanning speed. Pd did not cause significant improvement in tensile properties but did enhance corrosion resistance in 2 M HCl by shifting the corrosion potential into the passive region of Ti64. The current work suggested that the new approach is a feasible route of synthesising modified alloys with both chemical and microstructural homogeneity as well as improved performance for biomedical application.

1. Introduction

Selective laser melting (SLM) is one of the additive manufacturing technologies that enable fabrication of complex freeform geometries directly from computer-aided design (CAD) models. The technology is

* Corresponding author.
E-mail address: QiuC@cardiff.ac.uk (C. Qiu).

http://dx.doi.org/10.1016/j.matdes.2016.07.055
0264-1275/

particularly attractive for manufacturing biomedical components and structures as it allows for new complex designs that could enhance both mechanical and biomedical compatibility. So far, it has been used to fabricate a number of complex biomedical parts and structures including various porous implants [1–11], femoral components [12], human vertebra components [4] and dental parts [13]. A number of studies suggest that the selectively laser melted implants show excellent biocompatibility [1–7].

At the same time, SLM is believed to be a promising method for synthesis of new composites or modified alloys. Recently, this method has been used to prepare a number of composites for different applications [14–18]. Vrancken et al. [14] used this method to process mixed powder of Ti64 and Mo and suggested that the as-fabricated samples show tensile properties that are equal to or better than conventional β-titanium alloys. Attar et al. [15] synthesised in- situ Ti–TiB composites by SLM of milled Ti-TiB_2 which were found to show refined grain structure and significantly improved tensile strengths although the ductility was degraded to some extent. Gu et al. [16–18] developed TiC/AlSi10Mg nanocomposites with improved microhardness and tensile strengths and TiC/Ti nanocomposites with enhanced wear resistance by SLM. The report on using this new technique to enhance performance of existing biomaterials such as their corrosion resistance and biocompatibility, however, is lacking.

The key step to produce chemically and microstructurally homogeneous composites through SLM is powder mixing. So far, most of the powder mixing has been performed by ball milling which could easily damage the sphericity of original base alloy powder particles and also does not guarantee homogeneous distribution of the additive particles [14–16]. Very often, agglomeration of additive particles (especially nanoparticles) could still be observed and the added fine particles are usually separated from the main alloy powder particles after mixing [14–16]. These factors will all affect the distribution of additive particles among main alloy powder particles during the powder spreading stage of the SLM process and thus affect the consistency of microstructure and properties. An effective powder mixing method should not only give rise to homogeneous distribution of mixed powder particles but also keep the main alloy powder particles intact after mixing, particularly retaining the regular/spherical particle morphology that is preferable for SLM. Ideally, the additive particles should develop good bonding with main alloy powder particles after mixing so that they could be homogeneously spread with main alloy powder particles during SLM. This is particularly important for synthesis of a composite or modified alloy where the additive material is at low level. If the mixing method is not sufficiently effective, the additive material will not be widespread throughout the main alloy powder particles and the resultant SLM-built component. There are a number of such cases where the additive material is at low level in the field of biomaterials, for example, Pd-modified titanium and its alloys where Pd is usually added at a level of 0.04–0.25 wt.% [19,20]. Low level addition of Pd or other platinum group metals to titanium and its alloys is an effective way to improve corrosion resistance in a range of media, particularly reducing acids [21–24]. The conventional manufacturing route (casting + forging + machining) involves considerable waste of materials and expensive machining, which makes the production of Pd-modified titanium alloy parts for a limited number of applications expensive and time consuming. In the current study, a new powder mixing technique which involves no use of balls but only the use of mechanical centrifugal forces and has been proven to be effective in mixing different powder particles to a very homogeneous level within a short time (several minutes) and is capable of developing good bonding among different types of powder particles [25], has been used to mix Ti64 and Pd powder particles. The mixed powder is then processed by both SLM and HIPing, the latter being used both to remove porosity from SLM-made components and because it is another effective net-shape manufacturing technology when combined with modelling [26,27]. Samples were characterised in terms of porosity, surface structure, microstructure, mechanical and chemical properties. Throughout this study, the feasibility of the proposed new route in synthesising modified biomaterials will be discussed.

2. Experimental

The base alloy powder used in this study is Grade 5 gas-atomised Ti64 powder supplied by TLS Technik in the size range of 45–75 μm. The as-received Ti64 powder was doped with 0.2 wt.% Pd by Johnson Matthey (JM) using a proprietary powder mixing machine that involves the use of dual centrifugal forces as shown in Fig. 1. The machine mainly consists of a bottom plate and a basket set up on the plate in a slanted angle. Powder is loaded in a container which is then placed in the basket prior to mixing. When it runs, the bottom plate rotates clockwise around its central axis at an extremely high speed (up to 3500 r/min) while the basket rotates anti-clockwise at a quarter of the rotation speed of the plate. As such, two dual asymmetrical forces are created which drives the powder mixing. In the current study, the powder was mixed at a rotation speed between 2500 r/min and 3500 r/min for only several minutes. The as-received Ti64 and mixed Ti64 and Pd powder were subsequently processed using a Concept Laser M2 Cusing SLM system which employs an Nd:YAG laser with a wavelength of 1075 nm, a maximum laser output power of 400 W and a maximum laser scanning speed of 4300 mm/s. In the current study, 10 × 10 × 10 mm cubic samples have been fabricated at a constant laser power of 400 W but with different laser scanning speeds ranging from 1300 mm/s to 4300 mm/s. All the samples were fabricated using an "island scanning" strategy which has been detailed elsewhere [28]. Selected powder samples and SLMed samples were also hot isostatically pressed at 930 °C/100 MPa/2 h followed by furnace cooling for comparison.

Samples were ground using grinding papers successively from 240 grit up to 2500 grit before being polished using 3 μm diamond suspension and finally activated colloidal silica solution and examined using an optical microscope (OM) and a JEOL 7000 FEG-SEM (scanning electron microscope) to reveal the size, distribution and morphology of pores. Tessellated micrographs each containing tens of frames were used to study the porosity distribution over large areas. The porosity area fraction (Af) was quantified using ImageJ. Samples were further etched in Kroll's reagent containing 50 ml distilled water, 25 ml HNO3 and 5 ml

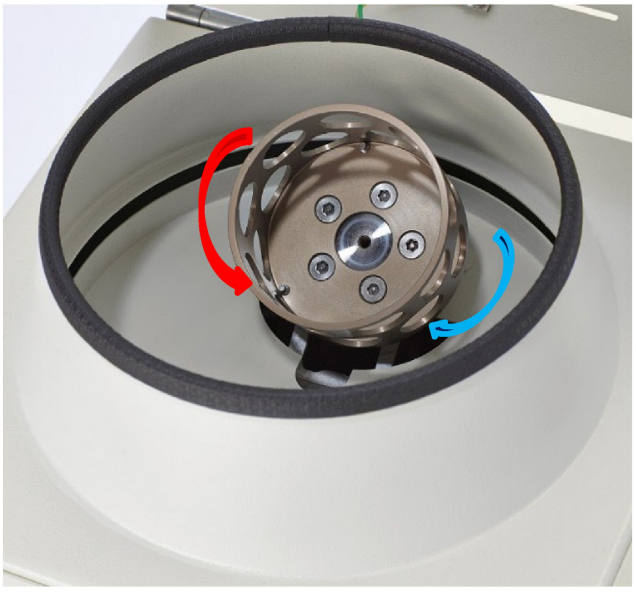


Fig. 1. A photo showing the new powder mixing machine used in the current study. The arrows show the rotation of bottom plate and the basket along their axes in different directions.