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Characterization of heat treatment-induced pore structure changes in cold-sprayed titanium

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ABSTRACT

Two X-ray computed tomography (CT) datasets have been acquired for a cold-sprayed titanium sample before and after heat treatment. The datasets were collected with a beam energy of 30 keV at the Australian Synchrotron. Three-dimensional (3D) distributions of porosity in the Ti sample were reconstructed using a data-constrained modelling (DCM) technique. Quantitative analysis indicated that the heat treatment caused morphological changes to the pores and a small decrease in the overall porosity. After heat treatment, some fine porosity disappeared while the large porosity regions were essentially unaffected except for a change towards a more rounded pore shape. Interconnectivity between pores was reduced, which has implications for sealing and trapping of contaminant gases in cold-sprayed parts. The characterization technique and the workflow presented in the paper are applicable to non-destructive 3D characterization of other materials.

1. Introduction

Cold spray is a method for the solid-state deposition of metals. It involves accelerating powder particles towards a substrate surface within a supersonic inert gas jet. Bonding occurs due to adiabatic shear instabilities at the particle interface caused by high-strain rate deformation during impact [1–3]. Cold spray is used for depositing coatings, repair and reclamation of worn parts and for additive manufacture (AM). Depending on the material being sprayed, deposits may be fully dense or contain some residual porosity.

Titanium is a metal with attractive properties, including low density (4.506 g/m^2), corrosion and oxidation resistance and biocompatibility. The recent availability of lower cost Ti powders via alternative production routes is a further driver for more widespread adoption [4,5]. Cold-spray additive manufacture of titanium components has been the subject of considerable interest [6–8].

However, titanium has limited ductility compared to face-centered cubic (fcc) metals such as copper and aluminium due to the hexagonal close-packed (hcp) crystal structure of its alpha phase. Consequently, Ti particles do not deform to the same extent upon impact, and some porosity generally remains [9,10]. This porosity may or may not be of concern, depending on the final application and the nature of the porosity, i.e. whether or not it forms a fully interconnected, open network.

A further consideration is that to improve the strength and ductility of the sprayed material, a heat treatment procedure is generally employed, at temperatures leading up to the α-β transition (882 °C) or slightly above [10]. Heat treatment causes recrystallization of the as-sprayed microstructure, which contains high concentrations of dislocations and other lattice defects due to the severe plastic deformation that occurs during impact [11]. However, it has been observed that exposure of cold-sprayed titanium to these temperatures also causes changes in pore morphology and the overall pore fraction [12–15]. This heat treatment is essentially a sintering process, albeit at a lower temperature range than used in conventional powder metallurgy processing to reach full densification. The onset of sintering occurs with dissolution of the surface oxide film, which has been observed at around 550 °C [12]. Li et al. observed an increase in porosity following vacuum heat treatment of cold sprayed titanium at 850 °C for 4 h. They attributed it to undetectable, fine porosity at particle interfaces in the as-sprayed condition, coalescing to form larger voids during heat treatment [13]. In another study, heat treatment produced more uniformly distributed pores and improved bonding between Ti particles due to atomic diffusion [14]. Wong et al. reported pore shrinkage, reduction in overall pore fraction and an increase in cohesion strength between particles after annealing of cold-sprayed Ti-6Al-4V at 800 °C [15].

From a practical perspective, understanding the nature of the porosity before and after heat treatment is important, since if air or process

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gas (nitrogen) remains trapped, high-temperature diffusion of oxygen or nitrogen into the bulk can cause embrittlement. Changes to the bulk density will also have an effect on mechanical properties. A change from an open pore network to a closed structure will influence the performance of corrosion- or oxidation-resistant titanium coatings.

Various techniques such as optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been employed to characterize and visualize the microstructure of materials such as titanium alloys [16–21]. These methods are useful for quantitative microstructural investigation at very high spatial resolution (about 200 nm down to 0.1 nm). However, they are limited in that the information obtained only comes from the near-surface region or a thin slice of material. Although the overall 3D structure can be built up by serial sectioning, this approach is time-consuming and sample destructive [22–24]. Furthermore, sample preparation of porous materials by polishing is not straightforward and, if performed incorrectly, may cause artefacts that lead to misinterpretation of the pore fraction and morphology [13].

X-ray micro-computed tomography (micro-CT) is becoming a powerful tool for non-destructive 3D characterization of metallic materials [25]. Zahiri et al. used X-ray CT to study porosity in cold-sprayed titanium and were able to reveal the pore morphologies and poorly-bonded particle boundaries within a thin slice of material [26]. Synchrotron radiation (*SR*)-based X-ray micro-CT makes it possible for quantitative reconstruction of 3D absorption images with a higher resolution and speed [27–29]. In contrast to X-ray CT with a micro-focus polychromatic source, the beam hardening artefact can be totally avoided due to the excellent monochromaticity of the SR X-ray beam. The high photon flux helps to reduce the exposure time. Furthermore, combined with the image threshold segmentation method, SR-based X-ray micro-CT has been widely used in the quantitative characterization of physical structures in materials science [30–33].

Despite the progress that has been made, some problems remain in the application of the technique to material characterization. Firstly, it is hard to distinguish material phases with similar X-ray absorption and refraction properties by X-ray micro-CT and the image segmentation method. Secondly, the sizes of some fine structures in materials are smaller than the pixel size of the reconstructed micro-CT slice, which makes quantitative identification of these fine structures difficult. Such sub-resolution fine structure leads to the partial-volume effect: the intensity at a voxel is an integrated effect of multiple compositions in the voxel. In principle, this can be overcome by increasing the image resolution e.g. using nano-CT; however, the sample size then needs to be reduced accordingly [34]. A small sample size gives a poorer representation of the macroscopic whole.

A data-constrained modelling (DCM) technique has been developed that is capable of resolving the partial distribution of multiple compositions within the same voxel [35,36], using one or more CT datasets acquired at different X-ray energies. It has been applied successfully in characterizing and predicting the microstructure of a range of different materials, including the distribution of corrosion inhibitor particles in aerospace paint primers, compositional distribution in corroded zinc and the distribution of gold particles in nanostructured functional materials [37–39].

In this article, we have used synchrotron-based high-resolution X-ray micro-CT combined with the DCM approach for quantitative investigation of pore structure change in a cold-sprayed Ti sample before and after heat treatment.

2. Sample Preparation

The cold spray process was performed using a CGT Kinetiks 4000 system. Nitrogen gas was chosen as the particle accelerant. The gas was preheated to 800 °C at a pressure of 3.5 MPa before passing through a CGT 40TC tungsten carbide de Laval nozzle. Titanium powder was fed into the gas flow upstream of the nozzle at a feed rate of 2.5 kg/h.

The powder feedstock was commercial purity grade 2 titanium purchased from Plasma Giken (PG-PMP-1041). It was produced by gas atomization and had a predominantly spherical particle morphology. The particle size distribution was measured by the laser diffraction method with a Malvern Mastersizer X. The 10th, 50th and 90th percentile particle sizes were d_{10} = 14.5 μm, d_{50} = 29.5 μm and d_{90} = 47.4 μm, respectively.

The substrate was a disc of aluminium alloy AA6061 with 110 mm diameter. It was held on a rotating chuck and spun at 500 rpm while titanium was deposited onto the flat face. The cold spray gun was controlled by an ABB 2600 6-axis robot, with the nozzle kept perpendicular to the substrate surface. The robot was programmed to move the spray gun perpendicular to the axis of rotation at a traverse speed that was at all times inversely proportional to the distance from the rotation axis. The gun was periodically moved back so as to maintain a constant 30 mm standoff distance between the nozzle and the deposit surface as the deposit grew. The resulting CP titanium deposit was 95 mm in diameter and 20 mm high. This spray method has been developed to allow even build up on a flat surface while maintaining a high relative speed between nozzle and substrate so as to minimize the detrimental effects of sample heating by the gas jet. Large cylindrical blocks of titanium > 1 kg have been thus produced [40].

The density of the cold sprayed disc was determined using the Archimedes water immersion method [9]. Three measurements of sample weight were made using a 4-decimal point balance; dry (after oven drying at 110 °C), suspended in a bath of distilled water at room temperature, and saturated (directly after removal from the water bath). The volume fraction of porosity was calculated from $1 - \rho_m/\rho_t$ where ρ_m is the measured density and $\rho_t = 4.506 g/cm^3$, the theoretical density of titanium.

A conical-shaped pin was prepared from the cold spray titanium disc for synchrotron X-ray micro-CT by the following method. Rectangular blocks were cut from the disc by electrical discharge machining (EDM). The block chosen for this study was 15 mm from the central axis of the disc. The linear surface speed at this location was 0.79 m/s and the material produced there was homogeneous. This block was turned down to a 2 mm diameter rod. One end of the rod was manually ground down with progressively finer SiC papers, up to 1200-grit, while it was spun at 200 rpm to achieve a further reduction of the diameter. The resulting pin was 0.2 mm in diameter at the tip. The diameter was 0.5 mm at the thicker end of the imaged region.

Following the first synchrotron X-ray micro-CT scan (see Section 3.1, below), the titanium pin was heat treated. It was placed in a quartz ampoule, which was evacuated, then partially back-filled with argon and sealed. The ampoule was heated to 850 °C, held there for 4 h, and furnace cooled. The second CT scan was performed for the same sample after heat treatment.

3. X-ray Computed Tomography

3.1. X-ray Projection Image Acquisition

The projection images were acquired at the Imaging and Medical Beam Line (IMBL), Australian Synchrotron (AS). Only the top part of the sample was imaged due to the vertical beam size limitation.

A double-crystal monochromator of Si (111) was employed to generate the monochromatic X-ray beam at 30 keV from the wiggler source [41]. The photon energy was selected for optimal image quality, which is related to the beam penetration through the sample. An Optique Peter CCD detector with a pixel size of 6.5 μm was used to acquire the projection images. A 10 × optical lens was coupled with the detector to achieve an effective pixel size of 0.65 μm. The sample-to-detector distance was set to about 300 mm. A total of 1800 projections were collected during the 180° sample rotation. The exposure time for each projection was 2 s. To correct for inhomogeneity in the X-ray beam intensity profile, ten flat-field images were acquired immediately before