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Understanding the Microstructural Evolution of Cold Sprayed Ti-6Al-4V Coatings on Ti-6Al-4V Substrates

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Keywords: kinetic spraying, Ti-6Al-4V coating, microstructure formation, bonding mechanisms, electron microscopy, finite element modelling

Abstract

Rapid development of cold spray technology has made it a viable option to remanufacture and repair damaged engineering components made of Ti-6Al-4V (Ti64). This solid-state deposition process contributes to the distinctive microstructure of Ti64 coatings. In this study, the microstructural evolution of Ti64 from feedstock powder to coating as a result of high strain rate deformation is evaluated. TEM lamellae were extracted from the particle-substrate and particle-particle interfaces of a cold sprayed coating by focused ion beam milling and a comprehensive microstructural analysis was carried out. The feedstock powder is predominantly composed of martensitic lathes. The microstructure of the coating at the particle-substrate interface is noticeably different from the microstructure of the feedstock powder. Narrow regions consisting of nanometre-sized grains are observed in both the particle and substrate in the vicinity of the interface. Adiabatic shear instability under localized high strain rate deformation and heat accumulation are believed to be responsible for this observation. However, the martensitic structure is partially retained in the less deformed region of the particles, further away from the interfaces. The formation mechanism of the microstructure observed from the inner region of particle, at the vicinity of the particle-substrate and particle-particle interfaces respectively is discussed in the light of microstructural observations and finite element modelling.

1. Introduction

Titanium and its alloys have gained considerable attention in both academia and industry for their exciting properties such as high strength-to-weight ratio, corrosion resistance and

biocompatibility [1]. The alloy Ti-6wt%Al-4wt%V (Ti64) has been extensively used in aircraft engines and turbine blades in aerospace industries due to its excellent thermal stability at elevated temperature [2]. This alloy is also an important material in biomedical applications such as prosthetic implants [3]. However, the use of titanium and alloys is often limited by high raw material and manufacturing costs. Therefore, it would be more cost effective and environmental friendly to be able to repair and remanufacture damaged structural engineering components made of titanium alloys to extend their service lifespan. Additive manufacturing or coating techniques such as thermal spraying [4], cold spraying [5], and laser metal deposition [6, 7] are viable options to perform such remanufacturing and repairing work.

Cold spraying is a promising surface deposition technique where micron-sized particles are accelerated to supersonic velocity and subsequently impacted onto a substrate surface. The coating process and its outcomes are governed by a variety of parameters such as carrier gas type, gas pressure and temperature, powder size and morphology and nozzle design [8]. The process produces a coating with a high deposition rate resulting in compact coatings with high dimensional tolerance and minimal weak heat-affected zones. Therefore, the main advantages of cold spraying over conventional thermal coating processes are the possibility of preserving the initial phase and microstructure of the feedstock powder as well as minimizing the adverse effects on both coating and substrate from high temperature processes such as oxidation, undesired phase changes and chemical reactions [9, 10]. In addition, cold spraying has also emerged as an additive manufacturing process due to its high deposition rate and low processing temperature [11]. Owing to its versatility and economic feasibility, cold spraying has been applied to deposit a variety of materials such as metals, ceramics, composites and polymers [9].

The velocity of the particles in the supersonic gas stream during spraying is critical to attaining a sound bond of the particles with the substrate or between the particles. It has been shown that the adhesion of the particles to the substrate or prior deposits happens when the impact velocity exceeds a critical velocity but stays below the erosion velocity of a given particle-substrate combination [12, 13]. To date, adiabatic shear instability (ASI) is the most established theory for the bonding mechanism in cold spraying [14]. During the impact, a strong shearing force usually normal to the impact direction is introduced in the particle near the impact interfaces and provides a driving force for the ASI to happen – the deformation of parent grains and nucleation of dislocations lead to localised strain hardening while the majority of the impact energy is dissipated as heat that results in thermal softening of the materials. This eventually results in material instability (thermal softening dominates over strain hardening) and strain accumulation up to 1000% in a localised region [13, 15, 16].

In recent years, cold spraying of titanium and its alloys has been widely investigated by simulations and experiments due to their upsurge in use in many industrial applications [17-19]. Plenty of studies have been carried out to optimize the cold spraying conditions and understand the mechanical properties of cold sprayed titanium and Ti64 coatings [20-25]. However, only a few studies have been focused on the microstructure and bonding mechanism of the deposited cold sprayed particles and the resulting coatings. Vidaller *et al.* revealed that the ASI is more prominent and results in better bond strength for particle-substrate combinations having higher similarity in both material and mechanical properties [26]. Li *et al.* reported that metallurgical bonding is attributed to localized interface melting for both titanium and Ti64 coatings, as a result of the poor thermal conductivity of the materials that eventually leads to high interfacial temperature and ASI [27]. Goldbaum *et al.* revealed the formation of nanometre-sized grains at pure titanium splat-substrate interfaces due to grain recrystallisation during the impact using electron channelling contrast imaging

(ECCI) and electron backscattered diffraction (EBSD) [28]. With the aid of transmission electron microscopy (TEM), Kim *et al.* showed the presence of nanometre-sized grains at the warm-sprayed titanium splat-substrate interface as a result of dynamic recrystallisation (DRX) induced by severe plastic deformation, whereas the microstructure at the region away from the interface was similar to the feedstock powder [29, 30]. Birt *et al.* discussed the microstructure of the feedstock powder and the cold sprayed Ti64 coatings [31, 32]. Different microstructures were observed within a coated particle and they were attributed to the formation of the fine grains and remnant martensitic lathes from the feedstock powder [31].

In this work we perform a comprehensive study of the microstructural evolution from Ti64 feedstock powder to cold sprayed coatings by means of scanning and transmission electron microscopy. In order to understand the bonding mechanisms between (i) the cold sprayed coating and the substrate and (ii) particles within the coating, the local microstructure has been investigated from specific locations on the particles within the coatings. To draw a comparison, the microstructure of a single splat has also been studied. The microstructural evolution from the feedstock powder to the cold sprayed particles has been explained in the light of local plastic strain and temperature profiles within the particle with the aid of finite element modelling.

2. Experiment and finite element modelling

Commercially available Ti64 powder (Grade 23, Advanced Powders and Coatings Inc.) with a size range of 15 – 45 μm was used as the feedstock powder in the cold spray process to form Ti64 coatings on Ti64 substrates. The substrates, Ti64 (Grade 5) plates with dimensions of 50 mm x 50 mm x 4.3 mm (thickness) were obtained from Titan Engineering, Singapore.

Two types of samples were deposited, namely full coating (multiple layers) and splat sample (single particle or single layer). The Ti64 coatings were prepared with an Impact Spray

system 5/11 with a SiC spray nozzle from Impact Innovations, Germany. Prior to the cold spray process, the substrates were ground with P1200 grit paper followed by fine polishing with DiaPro 9 μm diamond suspension (Struers). The full coating was deposited with a set of cold spray process parameters developed in a previous study by Tan *et al.* [23], i.e. carrier gas temperature of 1000 $^{\circ}\text{C}$, carrier gas pressure of 45 bar, traverse scan speed of 500 mm/s, spray angle of 90° , raster step of 1 mm and stand-off distance of 30 mm. The splat sample was cold sprayed with a similar set of parameters to the full coating, except for a lower powder feed rate (1/10 of that for full coating) and larger raster step (15 mm), in order to obtain isolated individual Ti64 splats and particle clusters on the substrate. Nitrogen gas was used as the carrier gas for all cold sprayed samples. The thickness of the full Ti64 coating was ~ 2 mm.

Prior to characterisation, the cold sprayed samples were sliced into smaller pieces with dimensions of about 10 mm $\times$ 10 mm. The sliced samples were then mounted, ground and polished sequentially with P1200 grit paper, 9 μm diamond suspension and chemical-mechanical polishing with an OP-S colloidal silica solution (Struers) to obtain a mirror-like surface finish. All the samples were examined unetched in order to reveal the unperturbed microstructure within the particles using backscattered electron imaging. Secondary electron (SEI) and backscattered electron images (BEI) of the powder and the coatings were recorded with a JEOL JSM-7600F scanning electron microscope (SEM) equipped with a thermal field emission gun electron source, secondary electron and backscattered electron detectors. The composition distribution of the splat coating was determined using an Oxford X-MAX energy-dispersive X-ray spectroscopy (EDS) detector equipped on the SEM. Electron backscatter diffraction (EBSD) of the coating and substrate was carried out using an Oxford EBSD system with a 12 bit CCD detector with 640×480 pixels, mounted on a JEOL JSM-7600F SEM. The AZtecHKL software was used to analyse the EBSD data. The crystal

structure and phase information were examined using a Bruker D8 Advance X-ray diffractometer (XRD) with a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV with a current of 40 mA. The measurements were performed at a scanning speed of 1 °/min from 20° to 100° of 2 θ . The microstructure of the powder and coatings was also analysed using a JEOL JEM-2010 TEM and an aberration-corrected JEOL JEM-ARM200F TEM, both operated at accelerating voltages of 200 kV. The TEM lamellae were extracted from feedstock powder, particle-substrate and particle-particle interfaces using a FEI Nova NanoLab 600i focused ion beam (FIB)-SEM dual beam system with a Ga ion energy of 30 kV. A Pt protective layer was first deposited on top of the area of interest on the polished coating's cross-section to protect the coating from ion beam damage during the milling process. The TEM lamella containing the region of interest was then lifted from the sample cross-section, transferred to a TEM half-grid with an *in-situ* micromanipulator and subsequently thinned further using the FIB. The final polishing of the thin TEM lamella was done using a voltage of 2 kV and a current of 90 pA. TEM lamellae were prepared from four specific areas of interest, namely the feedstock powder, the particle-substrate interface at both the middle and periphery of a particle, and the particle-particle interface, as shown in supplementary information Fig. S1.

The finite element software ABAQUS/Explicit was used to simulate the impact of a single cold sprayed particle on a Ti64 substrate during the metal cold spray process, with the physical, thermal and mechanical properties of Ti64 taken from Lesuer [33]. The Johnson-Cook plasticity model was used to determine the effects of strain hardening, strain rate hardening and thermal softening on the equivalent plastic deformation resistance and a dynamic failure model was used to accommodate the large plastic deformations in cold spraying. Details of the simulation are provided in the supplementary information.

3. Results

3.1 As-received Ti64 feedstock powder

3.1.1 Morphology and phase identification

Given the major objective of this work was to understand the microstructural evolution from Ti64 feedstock powder to the cold sprayed coating, characterisation of the as-received feedstock powder was performed first. The SEM micrograph in Fig. 1a shows the morphology of the as-received Ti64 powder, which was produced by plasma atomisation. The powders are near spherical in shape and have smooth surfaces with minimal satellite particles. The XRD patterns in Fig. 1b reveal the phases present in the Ti64 feedstock powder, its cold sprayed coating and the substrate. It is observed that the cold-rolled Ti64 substrate contains both the equilibrium low temperature hexagonal close packed (HCP) α phase and the high temperature body centred cubic (BCC) β phase, as expected. On the other hand, the phase present in the powder and the coating is mainly the HCP α or α' phase with no peak from the BCC β phase visible. Our lab-based XRD was not able to easily distinguish between the α and α' phases because of the similarity between the two phases with only a very subtle difference (0.1 %) in their lattice parameter along the c-axis [34]. We have not attempted to distinguish these two phases in this work and will thus refer to them both as the α' phase, which is the most likely phase at room temperature.

3.1.2 Microstructure

Fig. 2a shows SEM backscattered images of an unetched individual Ti64 powder cross-section. These images were taken with a high beam current to allow the relatively weak channelling contrast between the different grain orientations to be seen. It can be observed that the microstructure in the Ti64 powder is mainly comprised of the martensitic α' phase.

The martensitic microstructure is characterized by a long, directionally branched lath structure. In Ti64 this is generally formed due to the rapid solidification of β grains above the β transition temperature with cooling rates higher than 18 K s^{-1} [35]. During the plasma atomisation process, molten Ti64 droplets rapidly solidify into powders at a typical cooling rate of $10^3 - 10^4 \text{ K s}^{-1}$ [36]. Therefore it is highly possible to obtain a fully martensitic structure in the powders at this high cooling rate. A higher magnification BEI of the powder cross-section is shown in Fig. 2b. It can be observed that the size of the primary martensitic α' lathes is around 200 nm in width with feather-like branched secondary lathes of less than 100 nm in size. Apart from the martensitic lathes, twin bands could additionally be seen in the Ti64 powder. These twin bands are also commonly formed in rapidly solidified Ti64 powders [32].

To further investigate the microstructure of the powder, a TEM lamella from a Ti64 feedstock powder was prepared using FIB milling (Fig. S1a). The bright field TEM image in Fig. 2c shows an overview of the TEM lamella extracted from the centre of a Ti64 powder of $\sim 34 \mu\text{m}$ in diameter. The microstructure observed in the powder is predominantly martensitic α' lathes. These martensitic lathes are preferentially orientated with a width of around 200 nm, which is in agreement with the BEI in Figs. 2a and b. The presence of martensitic α' lathes in the Ti64 powder indicates that rapid solidification does not allow sufficient time for the β grains to transform into stable grains. Selected area diffraction patterns (SADP) were recorded from areas D1 and D2 (as shown in Fig. 2c). These diffraction patterns correspond to the α -Ti [001] and [100] zone axes respectively and confirm the HCP Ti structure in both the martensitic lathes and the twinned region. Fig. 2c also shows the twin bands present near the edge of the powder.

3.2 Cold sprayed splat and particle cluster

3.2.1 Microstructure and compositional information

The production of cold-sprayed coatings can be separated into two stages, the initial layer of particles impacting directly on the substrate followed by the subsequent layers of particles impacting on the prior deposits. Both good bonding of the particles onto the substrate and subsequently onto the prior deposits are essential for achieving a dense and well-bonded coating. The mechanism for bonding in many cold sprayed materials has been widely accepted to be due to ASI [10]. In ASI, interfacial bonding is induced by severe localized shear deformation and heat accumulation over a short period of time [13]. However, many factors such as the material properties of both the impacting particles and the substrate, as well as the particle velocity and impact temperature will determine the bonding quality of the cold sprayed particles.

To investigate the microstructural changes that occur when the cold sprayed particles first strike the substrate, while excluding or minimising the effect of subsequent layers of particles, we cold sprayed a substrate with sufficiently few particles that they formed a single layer with most particles isolated and only a few clusters formed by overlaps between particles. This type of sample is often termed "splat".

Fig. 3a shows a BEI of a cross-section of a successfully bonded Ti64 splat. The cold-rolled Ti64 substrate (bottom of Fig. 3a) consists of two different phases. The grains with darker contrast correspond to the HCP α phase while the brighter contrast, mostly along the grain boundaries of the α grains, corresponds to the BCC β phase of Ti64 [37]. The Ti64 splat (top of Fig. 3a) is heavily deformed as shown by the severe flattening of the originally spherical particle after the impact. The contrast within the Ti64 splat is relatively homogeneous, indicating that it consists of a single phase.

Three noticeable regions are observed along the interface between the Ti64 splat and the substrate: the narrow gap at the bottom centre of the splat (indicated by the red arrow on Fig. 3a), the well-bonded region at the periphery of the splat (blue arrows) and the material jet formation at the edge of the splat (green arrows). The central narrow gap is formed at the “south pole” [5] of the splat when it rebounds at the impact centre. This is commonly observed in cold spray deposition due to the elastic energy from the impact [30, 38]. The outflow of the material jet at the edge of the splat is indicative of the shear instability where thermal softening is locally dominant over strain and strain rate hardening at the interface during the impact by the particle. As the plastic deformation during impact takes place at the interface, it breaks down and removes partially, if not all, the oxide layers that might have formed at the surface of both the splat and the substrate, creating fresh surfaces for bonding between the splat and the substrate to occur. This gives rise to the well-bonded region (blue arrows in Fig. 3a).

In some areas of the sample described above multiple particles had landed near the same point forming a cluster. A BEI of a cluster consisting of four Ti64 particles is shown in Fig. 3b. All four particles in the cluster are flattened and plastically deformed. Both well-bonded interfaces and non-bonded regions can also be found between the particles. They are formed in a similar way to the interface regions found for the single Ti64 splat shown in Fig. 3a. In addition, it is also observed that there are two distinct regions visible in the BEI of each particle, a darker contrast region appearing at the upper part of the particle furthest away from the impact point and a brighter region appearing at the bottom half of the particle closer to the impact centre. They are termed the “textured” and “smooth” regions respectively, based on their microstructure as seen in backscattered images. This observation was also reported in a study by Birt *et al.* [31]. A higher magnification BEI of the particle-particle interface is also shown in Fig. 3c. The “textured” (darker) region of the particle appears to have some

twinning bands and initial martensitic structure while the “smooth” region appears to be rather featureless.

In order to identify any compositional changes, EDS compositional analyses were performed along the lines shown in Fig. 3b. From the EDS line scan shown in Fig. 3c, it is evident that the constituent elements Ti, Al, and V do not show any measureable segregation to the particle-particle interface. This EDS line scan also suggests that the composition is homogeneous both within the particle and across the particle-particle interface indicating that the “textured” and “smooth” regions have the same composition. An EDS line scan across the particle-substrate interface is shown in Fig. 3d. The two humps in the V line scan correspond to two areas of β phase in the Ti64 substrate. The β phase is richer in V, which is a β phase stabilizer in titanium alloys. It is noteworthy that the composition of the cold sprayed particle is close to that of the α phase in the substrate, indicating that the particle mainly consists of α' phase forming a solution with the β stabilizing elements. This confirms the finding from the XRD pattern from the coating in Fig. 1b showing predominantly HCP α' phase.

3.3 Ti64 cold sprayed coating

3.3.1 Microstructural characterisation by SEM and EBSD

Fig. 4 shows backscattered SEM micrographs from the unetched Ti64 cold sprayed coating cross-sections taken near the coating-substrate interface (Fig. 4a) and in the middle of the coating (Fig. 4b). These low magnification images show the general morphology of the coating cross-section and provide an overview of the particles’ morphology in the coating. The coating mainly consists of severely deformed and flattened particles. The characteristic features of cold sprayed Ti64 particles observed in Fig. 3b can also be seen in the thicker Ti64 coating (Fig. 4). Narrow gaps are found at most of the particle-particle interfaces in the coating, indicating that rebounding of particles takes place at the impact centre where the

particles strike. Meanwhile, there are also well-bonded regions adjacent to the narrow gaps that contribute to the adhesion of particles. It is noteworthy that both “textured” and “smooth” regions also appear in most of the particles in the coating. “Smooth” regions contribute to about 50% or more of the particle area. However, the volume ratio of “smooth” and “textured” regions depends on factors such as particle velocity, particle size as well as the impact point on the prior deposits. Fig. 4c shows a BEI of a typical particle-particle interface at higher magnification to clearly illustrate the “textured” and “smooth” regions. The impact direction is from top to bottom i.e. particle 1 collides onto particle 2. The two distinct regions are separated by the interface between particle 1 and particle 2. The “smooth” region at the bottom half of particle 1 appears to be featureless in the BEI. On the other hand, the “textured” region at top half of particle 2 partially retains the martensitic microstructure from the feedstock powder.

Fig. 4d shows an EBSD scan of an area either side of the coating-substrate interface. The striking feature of the scan is that only the substrate could be indexed by EBSD with virtually no indexing possible in the coating. This is reflective of the high degree of residual strain present in the coating of the as-sprayed aggregate that distorts the HCP α phase crystal lattice. Comparing the SEI (Fig. 4d-i) with the pattern quality (Fig. 4d-ii), inverse pole figure (Fig. 4d-iii) and phase maps (Fig. 4d-iv), it can be seen that no indexing was possible for a depth of about $3\mu\text{m}$ from the surface into the substrate, indicating the presence of deformation in the top layer of the substrate. The elongated grain structure resulting from the rolling of the substrate prior to cold spraying is visible from the inverse pole figure map. Here the surface normal is seen to be largely parallel to the $[01\bar{1}0]$ direction indicating a texture where the rolling direction is parallel to the c-axis of the HCP α phase.

The featureless “smooth” regions in the particles observed in the BEIs in Fig. 3 and 4, are believed to consist of equiaxed grains, with a random and independent orientation, as a result

of grain refinement. However, whether this is caused by dynamic recrystallisation upon impact by the particle could not be ascertained. EBSD was not able to provide structural information within the cold sprayed coating so instead we used TEM to understand the local microstructure in order to draw conclusions on the bonding mechanism.

3.3.2 Microstructural characterisation by TEM

Site-specific TEM lamellae were prepared by focussed ion beam milling from the particle-substrate and particle-particle interfaces to understand the microstructure at these regions, as shown in Figs. S1b-d. This technique provides a great advantage over conventional TEM sample preparation by electro-polishing or ion milling as it allows direct imaging of specific locations within the spray-coated sample to provide evidence for the microstructural evolution. This in turn helps us to understand the bonding mechanism of the cold sprayed Ti64 particle on the substrate. In the following sections, the local microstructure observed at various locations near the different interfaces are described.

Fig. 5 shows TEM images taken from the particle-substrate interface near the middle of a cold sprayed particle. The bright field TEM image in Fig. 5a provides an overview of the microstructure in both the particle and the substrate in the vicinity of the interface. There is a narrow crack around 60 nm wide at the interface (as indicated with blue arrows), formed by the rebounding of the particle at the impact centre. A similar crack can also be seen in backscattered SEM images, such as those shown in Fig. 3. The microstructure of the substrate is markedly different from that of the cold sprayed Ti64 particle. In the substrate large grains consistent with the microstructure of cold-rolled Ti64 are found with no nanocrystalline grains present. In the particle, close to the particle-substrate interface, the microstructure consists of relatively defect-free small grains (brighter regions) as well as some broken martensitic structure. In regions further away from the interface, more grains with an

increasing dislocation density (darker regions) are found. The green arrows in Fig. 5a marks the transition between these two regions. A SADP recorded from an area in the particle near the interface (area D1) is shown in Fig. 5b which indicates randomly oriented polycrystalline grains. This is clearly distinct from the single crystal diffraction pattern obtained from the martensitic lathes in the feedstock powder (Fig. 2c). The diffraction pattern in Fig. 5b corresponds to HCP α' Ti (supplementary information Fig. S4), even though this region contains sub-micron sized grains. Figs. 5c and d show bright and dark field TEM images from the area near the interface where the diffraction pattern is obtained. Comparing bright field and dark field TEM images, it is possible to identify some of the grain boundaries and defects in the microstructure. The grain size in the particle ranges from 50 to 200 nm. Fig. 5d shows that the broken or distorted grains are elongated perpendicular to the impact direction (parallel to the interface). Considering the random orientation of the martensitic lathes prior to the impact, this preferential alignment of the grains indicates a high lateral flow within the particle during the impact.

To evaluate the microstructure at an area where the interface is well-bonded, TEM lamella was lifted out from the particle-substrate interface near the edge of a particle. Fig. 6a shows an overview of the particle-substrate interface with the blue arrows indicating the exact location of the interface. Comparing with the particle-substrate interface from the middle of the particle (Fig. 5), this interface is much more difficult to see showing that there is strong bonding between the particle and the substrate. A diffraction pattern from area D1 is shown in Fig. 6a. It reveals the polycrystalline nature of the region and it also confirms the HCP Ti structure (as shown in the supplementary information Fig. S5). One discernible difference from the interface in the middle of the particle is that fine-grained regions are observed on both sides of the particle-substrate interface. The fine-grained regions are clearly visible in the bright and dark field TEM images shown in Figs. 6b and c respectively. The grain size of

50 nm or smaller, is significantly finer than the grains in the particle a little further from the substrate. A narrow fine-grained region is also observed in the substrate. Fig. 7a shows a high resolution TEM (HRTEM) image of the particle-substrate interface and the corresponding diffractograms from selected regions in the particle and the substrate adjacent to the interface. The image reveals the intimate bonding between the particle and the substrate with the thickness of the interfacial region being around 4 nm. On the particle side, a fine-grained region consisting of randomly oriented nanometre-sized grains is observed which is also verified by the diffractograms. A similar nanocrystalline microstructure is also observed in the substrate side and the diffractogram shows a pattern typical of the polycrystalline structure. In addition, interestingly a region exhibiting multiple twinning can also be observed on the substrate surface, demarcated by the white squared area "T". A higher magnification image of the twinned region along with the corresponding diffractogram is shown in Fig. 7b.

Fig. 8 shows a bright field TEM image taken across a particle-particle interface. The TEM lamella was prepared from an area where both "textured" and "smooth" regions are present adjacent to the interface to study the microstructural differences between them (Fig. S1d). There are in total three different regions included in this TEM lamella, labelled as P1, P2 and P3 that correspond to three different particles sampled within the foil as observed from the interfaces. The impact direction is from top to bottom. P1 is the top of a particle, P2 is a jetted part from an adjacent particle while P3 is the bottom of a third particle. The interfaces between the particles are indicated with blue arrows. Regions P2 and P3 appear to be relatively featureless, equiaxed and fine-grained. A diffraction pattern (Fig. 9a) from region P2 shows mostly continuous rings characteristic of nanocrystalline materials. Their spacing shows that region P2 has the HCP α' -Ti structure (supplementary information Fig. S6). Bright and dark field TEM images of this region are shown in Figs. 9b and c respectively and confirms that the grains in region P2 are fine and randomly oriented.

The particle-particle interface between regions P1 and P2 can be seen crossing near the bottom of Figs. 9b and c. There is a thin fine-grained layer in between the interface and region P1 (top of particle). Below this layer and visible in Figs. 8, 9b and c is the top of a particle (region P1), which has the martensitic lath structure. The microstructure in region P1 resembles the microstructure of the feedstock powder composed of remnant undeformed martensitic lathes. A diffraction pattern from this area (Fig. 9d) shows the grains are much bigger than for region P2. The long thin lathes can be identified from the bright field and dark field TEM images of P1 shown in Figs. 9e and f.

4. Discussion

Based on the evidence obtained from microscopy in Section 3, a scheme for the microstructural evolution of cold sprayed Ti64 powders can be proposed. As shown in Section 3.1.2, the original feedstock powder is formed entirely from martensitic α' lathes. We observe that when a particle hits a substrate the microstructure undergoes significant changes as compared to the original feedstock powder. The diagram in Fig. 10 shows the Ti64 particle microstructure that is found in the cold sprayed coating.

A high degree of plastic strain is accumulated in the deposited particles from the impact of the alloy particles. Since measuring the plastic strain at the particle-substrate interface experimentally is not yet feasible, finite element modelling of the impact of a single particle was used to get an idea of the strain induced. Figs. 11a and b show the distribution of temperature and equivalent plastic strain (PEEQ) at the bonding interface with the substrate 28 ns after the impact, assuming a Coulomb friction coefficient of 0.8 between the substrate and the particle. A very high strain of approximate 370% is found right at the interface between the particle and the substrate.

This single particle impact simulation shows that the maximum strain is reached at the lower periphery of the particle where ASI dominates. This high strain induces severe plastic deformation (SPD) at the vicinity of the particle-substrate (and hence also particle-particle) interface. In the particles, this is manifested through the refinement of the martensitic lathes. This refinement is most intense at the periphery of the particle and resulting in the formation of nanocrystalline grains as evident from the ring patterns in the SADP as shown in Figs. 9a and b.

The production of ultra-fine grained materials by SPD of metallic alloys through processes such as equal channel angular extrusion, multi-axial forging and high-pressure torsion, has been an important area of research [39-41]. Such ultra-fine grained materials possess an attractive combination of properties with high Hall-Petch type strengthening through grain refinement while simultaneously retaining an appreciable amount of ductility [39, 42]. Generally, the accepted mechanism for the formation of nanocrystalline grains in these processes is the creation of a very high density of dislocations, which then reorganize *in-situ* to form sub-grain boundaries that eventually rotate and transform into high angle grain boundaries (HAGBs) [43-45]. This process is termed “continuous dynamic recrystallisation” (cDRX) [45]. In cold spray, a similar level of strain is encountered. However, the additional factor is the extremely high strain rate that is not generally seen in the abovementioned SPD processes which are usually performed under a lower strain rates (typically 10^{-4} to 10^{-1} s^{-1}). The strain rates in cold spray process can reach up to 10^9 s^{-1} [13]. Therefore, a SPD process allows sufficient time for cDRX to take place while in the highly dynamic cold spray process, the occurrence of cDRX could not be ascertained given the extremely short impact time. Nonetheless, reorganisation of dislocations and grain recrystallisation could still happen to a certain extent, as observed at the interface of a cold sprayed titanium splat [28]. In addition, Zou *et al.* revealed the occurrence of cDRX in the cold sprayed coatings of low stacking fault

energy materials such as nickel and copper [46]. Further recovery and recrystallisation processes could be facilitated by the thermal treatment of the cold sprayed coatings [47].

Hence, we next compare cold spray with other dynamic high strain rate processes such as metal shot peening (MSP) and laser shock peening (LSP). The strain rates for MSP and LSP lie between $10^3 - 10^5 \text{ s}^{-1}$ and $10^6 - 10^8 \text{ s}^{-1}$, respectively. Thus, between these two processes, cold spray would be more akin to LSP. Recently Lainé *et al.* demonstrated the microstructural differences between these two processes in Ti64 [48]. In MSP, deformation is mediated by extensive twinning in addition to dislocations while in LSP the high dislocation density leads to the formation of dislocation tangles and low angle grain boundaries. The latter is quite similar to what we observed in the cold sprayed Ti64 particles.

The refined grain structure has also been noticed in cold sprayed aluminium alloy wherein grains with sizes ranging from less than 100 nm to a few hundred nanometres, were observed with high dislocation density in some grains [47]. Some of the dislocations could originate from the feedstock powder. It is probable that the interaction between the pre-existing dislocations from the rapidly solidified feedstock powders with the dislocations generated upon impact induces further grain refinement and recrystallisation processes near the impact interfaces [47].

In addition, a major fraction of the kinetic energy of the impacting particle is dissipated as heat. Given the very short impact time and thermal adiabaticity of Ti64, heat conduction is negligible during the impact. This in turn thermally softens the materials and gives rise to ASI that contributes to the subsequent grain refinement. Finite element modelling of a single particle impact is able to simulate and illustrate the local temperature rise at the interface. Several points in the high strain regions at the periphery of the particle, as labelled 'A' to 'G' in Fig. 11a, have been selected to plot their temperature history. As shown in Fig. 11c, these

regions experience a clear jump (termed “secondary” jump) in their temperature profile, where ASI takes place and aids in interfacial bonding [14]. These are the regions which experience maximum strain and heat accumulation and hence the greatest grain size refinement. Given that the melting temperature (T_m) of Ti64 is around 1933K, the maximum temperature at these regions reaches $\sim 0.8T_m$. With a very high density of dislocation nucleation, such a high homologous temperature can additionally assist in the process of recrystallisation and creation of fine grains.

The ultra-fine grained regions are seen to correspond to the “smooth” region in the BEI and also the featureless region in the TEM images. These regions are therefore located at the periphery of the particle near the bottom, at the high strain area. They are represented by the small circles in Fig. 10. This grain refinement does not only occur on the particle side - TEM images in Fig. 6 prove that the grain refinement happens in the substrate too. EBSD data in Fig. 4d also suggests that the high shearing at the substrate surface could possibly induce residual stresses and grain refinement within a thin layer in the substrate close to the interface. In the middle of the particle at the bottom, part of the kinetic energy from the impact is possibly relieved during the rebounding of the particle. Consequently, the impact energy is insufficient to cause further grain refinement but is still sufficient to break down and align the grains. It still appears as a “smooth” region in the BEI although the grain size in this region (50 – 200 nm) is not as fine as those at the particle’s periphery (≤ 50 nm). This incomplete refinement of grains is represented by larger circles in Fig. 10. In regions further away from the impact centre, the intensity of the deformation is largely reduced. Hence most of the martensitic lathes (represented by lines in Fig. 10) from the feedstock powder are retained, corresponding to the “textured” region in the BEI image.

The situation at the particle-particle interface is also shown in Fig. 10 when a second particle, “particle 2”, strikes a particle on the substrate, “particle 1”. The microstructure of the

“textured” region (top part of “particle 1”) and “smooth” region (bottom part of “particle 2”) is clearly different as in Fig. 8. Closer to the particle-particle interface there is a thin fine-grained layer in “particle 1” induced by the impact from “particle 2”.

Coupled with extremely high strain, both the substrate and the particle near the interface also experience very high strain rate deformation. Given the large dislocation density that results in the generation of the nanocrystalline structure, it is reasonable to assume that both homogenous nucleation of dislocations as well as dislocation glide occurs in the particles as well as on the surface layer of the substrate. In fact, under shock loading, it has been proposed that dislocations are homogeneously nucleated in the sample [49]; however heterogeneous nucleation from pre-existing dislocations also occurs [50]. Although not occurring in hexagonal but in face-centred cubic (FCC) crystals, glide of dislocations under shock loading occurs simultaneously on all available slip planes [51]. However, given the limited number of slip systems in HCP α -Ti a high volume fraction of deformation twinning was expected to occur in the substrate with a α - β microstructure under such very high strain rate loading. However, rather interestingly a few narrow bands of deformation twins were actually found in the substrate by HR-TEM imaging (Fig. 7b). This is an important finding in this context as virtually no twins were resolved by SEM-based EBSD or even conventional TEM. It was shown that under LSP only planar dislocations with a sub-grains was observed in the absence of deformation twinning [48, 52]. Also, deformation twins have a strong correlation with the grain size, small grains show a lesser propensity towards twinning than large grains.[53, 54] Given the nanometre-range grain sizes in both the cold sprayed coating and substrate near the interface, very little twinning was in fact observed. Even in the coating particles that undergo a higher deformation at the particle-particle or particle-substrate interface, compared to the substrate no deformation twinning was observed. With only a short time available for rearrangement, the nucleated dislocations have a very short mean free path

as they form the ultra-fine grain structure in the particles. However, it is to be noted that, strictly speaking, the particles consist of martensitic α' -Ti rather than close packed HCP α -Ti. In fact, α' -Ti is found in bulk Ti64 alloys that have been fabricated by additive manufacturing routes, such as selective laser melting (SLM) and electron beam melting (EBM) [55, 56]. Deformation studies on such martensitic Ti64 alloys until now only include conventional tensile or compressive testing [57, 58]. However, to our knowledge little to no data on either severe plastic deformation or shock loading of martensitic titanium alloys exists in the literature up to now. This warrants further work on the high plastic strain and strain-rate response of martensitic Ti phase to better understand the deformation mechanisms of the cold sprayed Ti64 splats.

5. Conclusions

In this study, the microstructural evolution from Ti64 feedstock powder to cold sprayed coating has been evaluated using electron microscopy. We observed from TEM images and diffraction patterns that the initial feedstock powder consists entirely of martensitic HCP α' lathes. These lathes are formed during rapid solidification during the plasma atomisation process used to prepare the powder. During cold spraying, the particles are subject to high strain rate deformation when they hit the substrate or prior deposit, so that the microstructure of the particle undergoes drastic changes. From a macroscopic view of the particle-substrate interface, three different regions of the particle-substrate interface are present – the narrow poorly bonded region at the bottom centre of the impact, the well-bonded region near the periphery of the particle and material jet formation at the particle's edge.

The microstructure in the particle near the particle-substrate interface consists of disintegrated martensitic lathes resulting from the high lateral flow within the particle during the impact. At the particle's periphery, regions with a grain size of less than 50 nm are found

on both sides of the interface. Thus the microstructure in these regions is very different from the microstructure of the original feedstock powder. Finite element modelling also indicates a very intense localized strain and a higher temperature at the side of the impact region as compared to the middle of the particle which is consistent with the more refined grains (≤ 50 nm) seen at the side (compared to 50 – 200 nm at the middle). Simulations of single particle deposition show a maximum strain of 370% and temperature of 0.8 times the melting temperature of Ti64 is reached at the particle-substrate interface. It is deduced that under the ASI, the martensitic lathes in the particles break down into finer grains. A fine-grained region is also found at the surface of the substrate resulting from the severe plastic deformation.

At the particle-particle interface, a similar situation is observed. The area adjacent to the interface of the impacting particle is subjected to high strain deformation and hence fine grains are formed at the bottom part of the particle. Remnant martensitic lathes are found in the top half of the particle away from the impact centre.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at:

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Fig. 1. (a) SEM micrograph of the as-received Ti64 feedstock powder and (b) XRD patterns from Ti64 feedstock powder (blue), its cold sprayed coating (red), and the Ti64 substrate (black).

Fig. 2. Backscattered SEM of an unetched Ti64 feedstock particle cross-section at magnifications of (a) 4,300 $\times$, (b) 10,000 $\times$ revealing the predominant martensitic structure in the particle. (c) Bright-field TEM image of a similar feedstock particle prepared by FIB milling showing the martensitic lathes and twin bands. Selected area diffraction patterns recorded from areas D1 and D2 are shown in the insets and confirm the HCP α' -Ti structure.

Fig. 3. (a) BEI of an unetched cross-section of a single Ti64 particle on a substrate with three regions of the substrate interface arrowed, the narrow gap in the middle of the particle (red arrow, 'm'), the bonded region (blue arrows, 'b') and the material jet formation at the particle's edge (green arrow, 'j'). (b) BEI of an unetched Ti64 particle cluster. EDS line scans were recorded at the particle-particle interface (Line 1) and the particle-substrate interface (Line 2). (c) EDS line scan from Line 1 and (d) EDS line scan from Line 2 along with enlarged backscattered images of the line scan areas.

Fig. 4. BEI of an unetched cross section of a Ti64 coated substrate at (a) near the coating-substrate interface, (b) inner coating region and (c) higher magnification image at a particle-particle interface. “T” refers to a “textured” region and “S” refers to a “smooth” region. (d) EBSD map of the coating-substrate interface. (i) SEI with the dashed line indicating the coating-substrate interface, (ii) band contrast (BC) map with superimposed high (black lines) and low (red lines) angle grain boundaries, (iii) inverse pole figure (IPF) map and (iv) phase distribution map (red and blue areas denote α and β phases respectively).

Fig. 5. (a) Bright field TEM image giving an overview of the particle-substrate interface near the middle of a particle. (b) Selected area diffraction pattern recorded at area D1 in the particle near the interface. (c) Bright-field and (d) dark-field TEM images showing the elongated grain structure in the particle adjacent to the interface.

Fig. 6. (a) Bright-field TEM image of the particle-substrate interface from the periphery of a bonded particle with a diffraction pattern from area D1 shown in the inset. (b) Bright-field and (c) dark-field TEM images showing the grain structure at the particle-substrate interface.

Fig. 7. (a) HRTEM image at the particle-substrate interface near the particle's periphery. Inset "p" and "s" show diffractograms correspond to the particle side and substrate side adjacent to the interface respectively. (b) HRTEM image of the twinned region (squared marked area "T") in (a) with an inset showing the corresponding diffractogram from this region.

Fig. 8. Bright field TEM image showing an overview of the particle-particle interface, where P1, P2 and P3 represent three different particles.

Fig. 9. (a) Selected area diffraction pattern recorded from the fine grained "jetted" part at the edge of a particle (region P2). (b) Bright field and (c) dark field TEM images taken at the interface between P1 and P2, with blue arrows indicating the interfaces. (d) Selected area diffraction pattern, (e) bright field and (f) dark field TEM images recorded from the top of a particle (region P1).

Fig. 10. Schematic representation of the microstructure of cold sprayed particles in a coating near the substrate. Small circles represent fine grains, large circles represent coarser grains and lines represent the martensitic lath structure.

Fig. 11. Modelling results showing distribution of (a) temperature and (b) equivalent plastic strain (PEEQ) at 28 ns after the impact of a cold sprayed particle on the substrate. (c) Temperature evolution in the high strain region at the particle-substrate interface with respect to time for points A to G.

Highlights

Understanding the Microstructural Evolution of Cold Sprayed Ti-6Al-4V

Coatings on Ti-6Al-4V Substrates

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Highlights:

- Ti-6Al-4V coating was cold sprayed onto Ti-6Al-4V substrate.
- TEM lamellae were made by FIB from powder and various interfaces in the coatings.
- Grain refinement was observed around the interfaces using EM.
- Formation mechanisms of microstructures in coated particle was revealed.
- FEM of particle impact showed high temperature and strain at the bonded periphery.

Graphical Abstract

Understanding the Microstructural Evolution of Cold Sprayed Ti-6Al-4V Coatings on Ti-6Al-4V Substrates

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