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Cold spray coatings are the sum of countless individual bonding events between single particles impacting on top of one another at high velocities. Thus, the collective behavior of microparticles must be considered to elucidate the origins of coating flaws at the scale of the particles and larger, or the dynamic evolution of the overall coating microstructure. Laser-induced particle impact testing (LIPIT) has been extensively used to study single-particle impacts, and in this work is adapted to study the accumulation of numerous particles with knowledge of each individual particle's impact parameters (particle size, velocity). The method reproducibly deposits stacks of gold particles (>20 particles) with different characteristic spectra of impact velocity. The quantitative single-particle data are analyzed in a correlative manner to the structure and flaws in the resulting stacks, providing some first semi-quantitative connections between, e.g., strain and recrystallization, or aberrant particle characteristics and defects. The results highlight opportunities for the study of many-particle phenomena in microparticle impact—from interaction of particles in cold spray to multi-step erosion processes—with a quantitative view of the behavior of single particles.

1. Introduction

Cold spray is an advanced manufacturing technology for coating, repair, and increasingly, the additive manufacturing (AM) of engineering metals^{1,2}. In cold spray, thick coatings are formed via acceleration of micron-sized particles to supersonic velocities, and their subsequent kinetic bonding onto a substrate upon impact. Fundamentally, a coating is the result of myriad bonding events of individual metal microparticles. Bonding of single particles is generally associated with a critical particle impact velocity—sufficient kinetic energy must be available to perform the plastic work necessary for solid-state bonding. Consequently, extensive studies of single-particle impacts have been conducted to better understand the fundamental aspects of these impacts.

Traditionally, single-particle impacts are studied with a wipe test. Here, a cold-spray plume with a known average particle size and velocity is rapidly translated across the substrate so as to deposit less than a monolayer of coating with isolated particles exposed on the substrate. This approach is straightforward and simple but lacks truly quantitative character, as the

individual particles' impact parameters (original size, inbound velocity, and temperature) are unknown. A more recent technique is laser-induced particle impact testing (LIPIT)^{3,4}, where single particles are accelerated by laser-ablation, mimicking the cold spray process in a tabletop optical setup. The synchronization of particle impact with high-speed videography enables the observation of the impact event and the measurement of quantitative data such as inbound and outbound velocities, and thus the kinetic energy dissipated in an impact event. The combination of LIPIT with post-mortem analysis by optical and electron-optical microscopy allows the study of particle deformation, fragmentation and bonding mechanisms. As a result, LIPIT has provided critical velocities for bonding of a wide range of metal particles^{3,5,6}, elucidated the influence of oxide layers^{7,8}, directly linked bonding to hydrodynamic jetting of material at the particle rims^{9–11}, mapped the deformation modes of particles¹² as well as the onset of erosion and melting^{13,14}, and revealed novel mechanisms for dynamic and static recrystallization upon or after impact ^{15,16}. LIPIT has thus proven to be an extremely insightful and versatile approach for the study of a wide array of phenomena related to single-particle impacts, as it provides a quantitative, single-particle view of the single-particle impact.

However, such single particle experiments do not speak to the inherently multi-particle phenomena known to influence cold-spray coating structure and properties. These include the tamping (densification) and peening (cold-working) of previously-deposited portions of the coating by subsequent particle impacts^{2,17}, the inclusion of pores between particles, or the fracture and erosion of coating material by particle strikes^{17–20}. These collective phenomena are typically studied only at a coating-level, but without access to the particle-level details that have proven so powerful in single-impact LIPIT experiments.

There is therefore a clear need for a single-particle view of the many-particle process that forms a cold spray coating, and our purpose in this paper is to provide a first step towards that goal. We employ LIPIT to study the collective behavior of gold microparticles forming many-particle deposits (up to 24 particles) through a coordinated sequence of individual shots with full LIPIT-accuracy on each shot. Such data are shown to offer better understanding of the missing links between inter-particle defects, coating microstructure, and individual particle behavior.

2. Materials and Methods

2.1. Laser-induced particle impact testing (LIPIT)

Detailed descriptions of the LIPIT setup have been published elsewhere²¹. Launch pads—the substrates that launch microparticles at high velocities—were composed of a 210 μ m thick glass substrate (Corning No. 2 microscope cover slip, 25 mm diameter) coated with a 90 nm thick chromium and 75 μ m thick polyurea layer. Polyurea precursors (Modified MDI Isocyanate curative, RCS Rocket Motor Components, and GCLink P-650, Chem Coast Incorporated) were mixed in a planetary centrifugal mixer (2 min, ARE-310, Thinky) in a mass ratio 1:2.4 (MDI:P-650) and then spin-coated (G3P-8, Cookson Electronic Equipment) at 750 rpm for 5 min. The PU films were cured at 85 °C for 24 hrs under vacuum. Gold microparticles (99.9%, Alfa Aesar, 200 mesh) were spread on the polymer layer using lens cleaning papers and a drop of ethanol. For impact-bonding experiments, gold targets were placed at a distance of 150-200 μ m from the launch pad. Two kinds of targets were used, Si wafers coated with ca. 100-nm thick, sputter-deposited gold films, and Si wafers electroplated with ca. 3- μ m-thick gold films (TSG-250, *Transene Company*).

Particle stacks, or "deposits", were formed by sequentially impacting and bonding particles without translation of the target in-between shots. To launch selected particles (9–20 μ m in

diameter) towards the target, an intense laser pulse (pulsed Nd:YAG, pulse width 10 ns, λ =532 nm) was focused onto the launch pad (30-mm focal length lens with a minimal focal spot size of 5 µm). Upon ablation of the metal film, rapid expansion of the generated plasma bulges the polymer film and in turn accelerates and launches microparticles towards the target. The particle speed was controlled by adjusting the laser energy between typically 0.4 and 0.7 mJ. The particle size was measured before launch. For reproducible impact location and successful build-up of many-particle coatings, reproducible alignment of particles in the center of the ablation laser beam is crucial. In previous versions of the system, a single imaging path was used for this task. For this study we used a second imaging path perpendicular to the first to render particle alignment more accurate²². The growth and fracture of deposits was also observed with the same imaging path used for particle alignment. The launch and impact of individual particles was imaged with a high-speed camera (SIMX16, Specialised Imaging), with a typical frame and interframe time of 5 ns and 45–95 ns, respectively. Particle velocities were measured from these image sequences. An error in velocity measurement of $\pm 5\%$ was estimated based on multiple re-measurements of a range of image sequences at the relevant interframe times. This fractional error is displayed by the error bars. A 10 μ s laser pulse (λ =640 nm) was used for illumination of 16 frames. In general, the magnification of all cameras was calibrated with resolution targets before experiments.

2.2. Analysis

The dimensions of particle deposits were measured with a laser scanning confocal microscope (VK-X250, *Keyence*). SEM was performed with a Gemini 450 instrument (*Zeiss*). Crosssections of deposits were prepared in a dual-beam FIB (Helios 660, *FEI*) with a typical final milling current of 9.3 nA.

3. Many-particle deposits with quantitative, single-particle impact data

In LIPIT, individual microparticles of known size are launched towards a target at up to 1000 m s⁻¹ while their impact velocity is monitored by high-speed videography (Figure 1a). The top image sequence in Figure 1b shows a gold particle, 14 µm in diameter, impacting a gold target at 358 m s⁻¹. The absence of a rebound indicates kinetic bonding of the particle to the target. Adhesion is expected at this impact velocity, as the critical velocity for bonding of gold particles has previously been measured to be on the order of 250 m s⁻¹ (for particles of diameter $16 \pm 4 \ \mu m$)⁵. In traditional single-impact studies by LIPIT, the target would now be moved to present a pristine impact site for the next test. In our case, however, the target is not translated in-between single shots. Thus, the next particle hits and bonds close to or on top of the previously adhered particle. A 3D deposit is formed upon the continued repetition of this process (Figure 1c). As the interparticle time is on the order of minutes, there is no accumulation of heat produced by plasticity; all particle launches occur under static, isothermal initial conditions. The formation of the particle stack is observed with two levels of temporal resolution. On one hand, the impact of every particle is resolved with high-frame-rate imaging. The bottom image sequence in Figure 1b depicts the impact-bonding of the 24th gold particle onto a previously deposited stack of particles. Just as with single-particle impacts, such an image sequence reveals inbound and rebound velocities of particles (if there is rebound). On the other hand, post-impact photography shows the growth of the entire deposit (Figure 1d). Importantly, the latter resolves fracture of the deposits (fracture typically occurs on a longer time scale than what the high-frame-rate imaging captures).



shot: 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 Figure 1. Many-particle deposition by laser-induced particle impact testing (LIPIT). a) In LIPIT, individual microparticles are launched towards a target by laser ablation of a sacrificial metal layer and subsequent, rapid expansion of a polymer film. Sequential impact at the same target location enables the deposition of coatings or stacks of many particles. b) Synchronized, high-speed videography is used for the direct observation of the particles' trajectory and impact and the measurement of particle velocities. The sequences capture the impact-induced adhesion of single microparticles on a pristine target (top) and a stack of many particles (bottom). c) SE-SEM micrograph of a deposit of 24 gold microparticles. d) Postimpact optical micrographs for each of the 24 shots show the growing deposit.

Typical deposits studied here contain 20-30 particles (9–22 μ m in diameter) and have an aspect ratio greater than one (**Figure 2**). The stack diameter of 30–50 μ m is 2–4 times the original size of the particles (9–22 μ m). The width of the deposit is caused by a combination of particle flattening upon impact and a lateral offset between particles. The offset, which can be as large as a particle diameter, is a result of the inherent experimental variability of launch trajectories in LIPIT. Conveniently, this natural variation simulates the range of particle offsets expected in actual cold-spray coatings.

In general, the quantitative view of every impact that builds a deposit is what crucially distinguishes the LIPIT approach from wipe tests or standard coating experiments. Based on single-particle data, the spectrum of particle sizes, velocities and dissipated kinetic energy of every coating can be measured. Figure 3 shows four successful particle stacks and the associated particle sizes and velocities (error bars: $\pm 5\%$) of every particle contained therein. The average particle velocities ranged from 328 ± 45 to 354 ± 37 m s⁻¹, well above the critical velocity $v_c=253\pm7$ m s⁻¹ for bonding of Au particles on a matching, flat, bulk substrate (reported in prior work for particles of size $D=16 \pm 4 \mu m$)⁵. However, with LIPIT, we can go beyond the averaged view and assess local variability within the stacks. For example, we measure that the lowest particle velocity for bonding was 249 m s⁻¹ for a 20-µm particle, that one particle impacted at only 169 m s⁻¹ and probably rebounded (unfortunately, the data is inconclusive as the possible rebound event occurred after the acquisition window), and that some particles impacted at >400 m s⁻¹. Based on this particle-specific data, in principle, it should be possible to track the location of the particle within the coating and correlate possible microstructural features associated with it. We turn our attention to such correlative analysis in the following sections.



Figure 2. Stacking of particles—lateral offsets. Particles are laterally offset within the deposits due to inherent experimental variability of launch trajectories in LIPIT. **a)** Top-view laser-scanning confocal micrographs of three particle stacks containing 23, 24, and 14 particles respectively (the third stack fractured upon impact of the 14th particle). The circles below indicate the size of the largest and smallest particle bonded within the deposit (original particle size). The fracture surface of the third deposit reveals three particles (colored), visualizing the lateral offset between particles. **b)** Corresponding line profiles along the vertical axis. The diameter of the deposits is 2–4 times the particle size.





Figure 3. Velocity and particle size spectra of deposits. a) SE SEM micrographs of intact Au deposits (Viewing angle 45°, no tilt correction). **b)** Impact velocities and sizes of all particles shot at the respective target to build the corresponding deposit (note that some of the slowest particles might not have bonded, of which we don't have evidence). Error bars for velocity: \pm 5%. The dashed line labels the average velocity and the purple band the standard deviation. $v_{cr, Au}$ =253 \pm 7 m s⁻¹ (black dashed line) denotes the critical velocity for bonding of single Au particles 16 µm in diameter⁵.

4. Impact-induced erosion of deposits

Impact-induced erosion of cold-sprayed coatings during deposition should be minimized for maximum deposition efficiency. Different types of erosion events are typically associated with three velocity regimes^{18–20,23}. Just below the critical velocity v_{cr} for particle adhesion, the

substrate may erode due to impacting but rebounding particles. At velocities larger than v_{cr} , particles start to adhere and a deposit is formed (with a deposition efficiency that increases with velocity). In this stage, previously adhered particles may be eroded due to impact-induced fracture (sometimes likened to grit blasting)¹⁷. At the upper end of the spray window, erosion of the coating and the substrate due to various high-energy-impact-induced phenomena is observed¹⁹. These high-velocity types of erosion—melting, hydrodynamic penetration and/or particle fracture—have been reported and quantified at the single-particle level in previous LIPIT studies^{14,24,25}. In this report, we can now observe erosion from the second, lower velocity-regime using LIPIT. The growth sequence in **Figure 4a** documents particle-by-particle buildup until shot 10. Yet, upon shot 11, fracture of the previously deposited material is obvious. The post-fracture micrograph in **b**) indicates inter-particle fracture occurred.



Figure 4. Fracture of a deposit upon impact. a) Sequence of optical micrographs that show the growth and fracture of a particle stack. **b)** Corresponding post-mortem SE SEM micrograph indicating inter-particle fracture (viewing angle 45°).

Fracture has been observed during the build-up of a number of deposits (**Figure 5a**). Sometimes, deposits fractured, continued to grow, and fractured again (the black arrows mark impacts that led to erosion as observed in the optical microscope). In almost all samples, the first fracture occurred before the 12th particle. At this stage, the deposits have an aspect ratio of roughly 0.5 or lower (as deduced by comparison to Figure 2, where deposits built from >20 particles have an aspect ratio of approximately one). Average particle velocities in fractured deposits—274±31 to 329±68 m s⁻¹ (purple band)—were consistently equal to or below the range of average velocities of successful coatings (green band, >328 m s⁻¹). From this data it is concluded that continuous buildup only occurred for an average particle velocity of ca. \geq 330 m s⁻¹. Below this value, deposits invariably fracture. Notably, an average particle velocity of >328 m s⁻¹ is well above the critical velocity $v_c=253\pm7$ m s⁻¹ for bonding of individual particles (D=16 ± 4 µm)⁵ (and so are the velocities of most individual particles in these coatings). This data thus suggests the existence of a minimum velocity for material buildup that is higher than the average critical velocity for bonding of single particles.

Multi-particle LIPIT experiments such as these may be particularly useful to quantify the contribution of erosion to the deposition efficiency at the lower end of the deposition window. In that range, researchers report that the deposition efficiency of the cold-spraying process is markedly below 100% after the onset of deposition, and only gradually increases with particle velocity within a transition zone that can span a few hundred meters per second²³. Erosion due to blasting might contribute significantly to the slow increase in coating efficiency. But in cold-spray experiments, this contribution is challenging to decouple from the effect of particle-size-dependent critical velocities for adhesion⁶ which—in combination with the ever-present size distribution within powders—naturally causes a gradual instead of a steep increase in deposition efficiency²³. In addition, differently sized particles would be expected to have different velocities and temperatures as well, so the notion of a single 'critical velocity' at the particle level is very challenging to map to coating efficiency. LIPIT, by contrast, offers potentially straightforward decoupling of these effects (as particle size, velocity and temperatures can be separately controlled). In fact, our experiments suggest that erosion could

lower the deposition efficiency by several dozen percent—Figure 4 and Figure 5 indicate that material loss by erosion could be more than 50%.

Despite the promise of the current technique, two points need to be taken into consideration when comparing the fracture events seen here to the particle blasting that can occur in cold-spray. First, and most importantly, these LIPIT deposits lack lateral constraints as they are built in isolation on a flat substrate. Deposits might thus experience impact-induced stress-states that are not observed in laterally-constrained cold-spray coatings (even though fracture occurs at low aspect ratios of ≤ 0.5). Future experiments might consider the addition of a random raster within a defined region in the plane to broaden the width of deposits and address this issue. Secondly, although we have no direct evidence to this effect here, there is a chance of organic contamination from the polymer launch pads used in the present LIPIT experiments, which may lower the bond quality. Deposition of organics atop of adhered particles and particle stacks is obvious in the SEM micrographs, and such layers may clearly have an undesirable effect for future bonding events, which are quite influenced by interface layers at the particle level^{7,8,26}.



Figure 5. Velocity spectra suggest a critical velocity for effective coating buildup. a) SE SEM micrographs of fractured Au deposits (Viewing angle 45°, no tilt correction). b) Corresponding velocity and size spectra. The vertical green bar denotes the range of the minimum and maximum average velocities of the deposits from Figure 4, all of which were coherent deposits. The dashed purple line and band denote the average velocity and their standard deviation for each of the present experiments, which failed to produce a coherent deposit. Black arrows mark impacts that led to fracture as observed in the optical microscope. It can be noted that continuous buildup of the deposits is only observed for an average particle velocity of ca. \geq 330 m s⁻¹. Significantly below this value, deposits fracture invariably. This suggest the existence of a critical velocity for material buildup that is higher than the average critical velocity for bonding of a single individual particle (the critical velocity for bonding of single Au particles, 16 µm in diameter⁵, v_{cr, Au}=253±7 m s⁻¹ is marked by a dashed, black line).

5. Inter-particle porosity

Cross-sections of cohesive deposits—prepared by focused ion beam (FIB) milling—often reveal internal porosity (**Figure 6a**). As this porosity is characteristically found at particle-particle interfaces, we attribute these flaws to incomplete bonding. In principle, the degree of bonding might be correlated to the kinetic parameters of the particles involved. For example, one could make a first hypothesis that the pronounced gap in Figure 6a (black arrow) has been formed because of insufficient impact velocity of the group of particles located directly above the gap. In general, low velocity should reduce both bonding of the first particle, and the degree of peening that could promote closure of any porosity in the vicinity. Other related hypotheses

could seek such a correlation with, e.g., both the size and velocity of the particles, or the kinetic energy of the particles. With the single-particle data provided by LIPIT, we proceed to develop an approach to quantitatively test such hypotheses.

First, the location of the pores throughout the volume as a function of deposit height is extracted by analysis of four cross-sections cut at approximately equidistant positions (approximately at 1/5, 2/5, 3/5, and 4/5 of the deposit diameter). Their projection onto a single plane is shown in **Figure 6b**. This spatial mapping of inter-particle flaws has been performed for all cohesive deposits (**Figure 7a, c, e, g**).

Because we are not able to map individual particles in the LIPIT sequence with exact positions in these stacks, we instead attempt to map *relative* positions in the stack to the particle sequence. Specifically, we plot the LIPIT particle characteristics as a function of accumulated total particle diameter of all the launched particles (**Figure 7b**). Here, the width of each horizontal bar corresponds to the original particle diameter and represents the relative contribution of each particle to the total height of the deposit. Then, this plot is scaled to the actual height of the deposit by aligning the bottom end with the lowest point of the bottommost particle, and the bottom edge of the top data point with the bottom edge of the topmost particle (approximate, average position). With this display, we can connect coating flaws to a group of particles that have interacted with the relevant portion of the deposit, even though the exact particles involved in the production of the flaw cannot be pinpointed.



Figure 6. Volumetric mapping of inter-particle porosity within deposits. a) SE SEM micrographs of FIB cross-sections cut at roughly equidistant intervals across the width of the deposit. Inter-particle porosity is highlighted in red. **b)** Overlay of the porosity detected in four cross-sections and its condensation into a qualitative plot of volumetric porosity versus height of the deposit.

With this approach we can proceed to test the hypotheses laid out above, seeking correlations between areas of increased porosity with anomalies in the kinetic attributes of the relevant particles. The first hypothesis above would connect particle velocity with flaws, so particle absolute velocity is the first of the quantities plotted for each deposit (Figure 7b, d, f, g). Yet, the critical velocity for particle adhesion is known to be particle-size dependent. Correspondingly, it should be assumed that the percentage of bonding and extent of peening may be a function of not only velocity but also particle size. Using LIPIT of Al and Ti, Dowding *et al.*⁶ have experimentally verified an exponential scaling of the critical velocity v_{cr} with particle diameter d, $v \propto d^{-n}$, with an approximate scaling factor of n=-0.2. Thus, we present the particle velocities normalized by $d^{-0.2}$ in a second plot. Finally, we also calculate the kinetic energy of impacting particles ($mv^2/2$).

Interestingly, in Figure 7, pronounced dips in velocity (or $vd^{0.2}$) never co-locate with notably higher degrees of porosity. Along the same lines, the concentration of wide horizontal gaps (c,

e, g) does not align with particularly low impact velocities. It is thus concluded that a low velocity alone does not cause pronounced porosity, even when that velocity is normalized by particle size in a manner expected to correlate to bonding characteristics. However, the data more convincingly suggest a correlation between porosity and low kinetic energy of particles. In both, d) and f), the relative position of extensive porosity aligns with a sequence of four to five particles of below-average kinetic energy (<1.6 µJ, and as low as 0.8 µJ). The same correlation however is not found in h). Further, it is clear that no threshold kinetic energy for poor densification can be defined in the present dataset. Multiple consecutive impacts of similarly low kinetic energy, for example in b) at a height of ca. 140 µm, or d) at ca. 170 µm, are aligned with areas of reasonably high density. Consequently, kinetic energy-if indeed correlated with porosity—can only be one factor in bonding or densification. Likely, other local conditions, such as precise offsets of impacts, specific stacking sequences, or specific deformation behavior of particles, need to be considered. For example, it seems possible that a pronounced, local protrusion-for example the inclusion of a below-average-size, satellite particle, or the upward extrusion of material-in combination with a local dip in kinetic energies may have favored the development of the extensive gap in Figure 7e (Supplementary Figure 1).

In summary, it does seem clear from this data that individual particle-velocity by itself is not a factor in porosity development, also when taking into account the possible error in spatial mapping of pores to particle velocities (a shift of LIPIT datapoints a few particle diameters up or down the height of the deposit should be considered as a possible error). In b), the porosity is homogeneously distributed despite significant variations in velocity. In d), the first, second and fourth particle are of low velocity, but in the corresponding cross-sections (c) at least three particles can be counted below the gap. As this is likely an undercount, the low-velocity particles are not likely spatially correlated with the porosity. And in f), low-velocity particle number eight is within the vicinity of the accumulation of flaws, but multiple particles must have formed the associated, porous volume (and particles seven and nine are of above-average velocity).



Figure 7. Correlation between inter-particle defects and individual impact characteristics. a, c, e, g) Representative SE SEM cross-sectional micrographs of cohesive deposits (tilt corrected). The red porosity map is an overlay extracted from four, roughly equidistant cross-sections. **b**, **e**, **f**, **h**) Velocity, velocity normalized by $d^{-0.2}$, and kinetic energy (mv²/2) of all individual particles plotted as a function of cumulative particle diameter—the width of each bar indicates the original diameter of individual particles before deposition. The plots are scaled to the total height of the deposit: the bottom end of the plot is aligned with the lowest point of the bottom-most particle. The relative position of the detected porosity is mapped to the left of each graph. The average velocity and kinetic energy is indicated by a dashed, blue line. This form of display suggests a correlation between the occurrence of porosity and low kinetic energy of particles (but notably, no correlation to particle velocity).

6. Microstructure evolution

Cold spray coatings typically feature heterogeneous microstructures that are characterized by extreme strains, strain rates and strain gradients. Deformation, work-hardening and the resulting recovery and recrystallisation-both dynamic and static (during deposition or a postdeposition heat treatment)—are the processes that underly the formation of a typically complex, bimodal grain structure. Based on the analysis of full coatings as well as individual particle splats, the heterogeneous microstructure is generally attributed to a strongly heterogeneous distribution of strain within deposited particles^{2,27}. FEM simulations²⁸ and experimental data¹⁵ estimate the strain in peripheral regions of particles to be 0.5 to 5 times higher than in the center. While the importance of the intra-particle strain gradient cannot be underestimated, one needs to assume that there are also significant differences in degree of deformation between individual particles that originate from size- and spray-dependent variations in impact-velocity. In general, the size-dependence of particle acceleration can cause a variability of impact velocity by tens of percent (and with it, strain) within a particle batch of typical size distribution^{18,29}. Further, pronounced differences in particle deformation for impacts at the center and near the rim of the spray have been demonstrated³⁰. However, establishing the effect of the significant velocity distribution on the final microstructure is difficult at the coating level. The comparison of averaged kinetic measurements to microstructure data that captures the post-event sum of hundreds of impacts is missing the particle-specific kinetic data that could link impact parameters to local strains and local microstructure evolution. Here, we propose that stacks of well-defined particle streams accelerated and quantified by LIPIT can potentially present a simpler environment to study the particle-scale evolution of the cold-sprayed microstructure.

Figure 8 presents three characteristic microstructures that are found within all particle stacks: first, volumes of heavily deformed, micrometer-scale grains that represent the original but work-hardened microstructure of the particles (Red. The large lattice strains show as distorted, gradient grayscale contrast in the BSE SEM micrographs); second, volumes of large, stress-free grains that must be the result of extensive grain growth upon recrystallization (Blue); and finally a seemingly transitional regime (Orange) that contains, on one hand, what appear to be well-formed recrystallization nuclei (areas with typically sub-micrometer grain size and low to medium distortion (black arrow in b)), and on the other hand, large regions of heavy deformation of the prior microstructure (red arrows).

These three microstructural types correspond rather well to the conventional individual stages of many manufacturing processes that involve significant strain and recrystallization. The heavily strained, large crystallites (red) that most likely are residual from the original particles correspond to "stage 1": accumulation of plastic deformation in the prior micron-scale grains. At the other end of the process, fully recrystallized, stress-free volumes (blue) correspond to a conventional "stage 3". And the areas that show signs of stress-relaxation by recovery and nucleation of new, submicron-scale grains (orange) likely belong to an intermediate "stage 2". One open question is the duration and timing of the transitions between these stages. In contrast to the cold-spray process, in LIPIT there are minutes between individual impacts, and the temperature of the deposit can be assumed to be room temperature for all but the shortest times (no post-deposition heat treatment was performed). Consequently, no particular time or temperature can be pinpointed as the trigger for recovery and recrystallization. Related to the question of timing is the question of whether there are multiple cycles of the sequence—whether stage 3 material is reworked by subsequent impacts to produce a microstructure of stage 1 that then can undergo the same cycle again. This of course would require

recrystallization in-between impacts, not after, and this may be less likely in room-temperature LIPIT experiments than in cold spray.



Figure 8. Recrystallization and grain growth. a) BSE SEM micrograph of a FIB-milled cross-section of a deposit (tilt corrected). Three distinct microstructures—found in all deposits—are highlighted in a) and isolated in **b)** Red: areas of large grain size with high defect density and lattice strains (characterized by distorted, gradient grayscale contrast)—the original but heavily deformed microstructure of the particles. Blue: fully recrystallized, large, stress-free grains. Orange: intermediate stage that contains what appear to be well-formed recrystallization nuclei (black arrows), as well as large regions of heavy deformation of the prior microstructure (red arrows).

An analysis of the volumetric distribution of these three microstructures in two particle stacks is made by comparison of the same four cross-sections per stack already used before in Figure 7 (Figure 9a, b, e, f, Supplementary Figure 2). Several interesting observations are apparent from these views. First, the initial but heavily strained microstructure is most prevalent in the top-most particle. This is an important point when thinking about single-particle studies of microstructure evolution in cold spray^{15,31,32}. Although a single particle impact produces considerable deformation with attendant interesting details, a substantial portion of its microstructural evolution history is certainly a product of the subsequent peening it receives. In fact, it may be difficult to connect single particle observations of, *e.g.*, recrystallization or other structural change with the microstructures seen in cold spray generally in light of this observation.

Second, it is curious to note that some of the deformed prior-particle microstructure (red) survives all the subsequent deformation imposed from downstream impacts, and remains in lower portions of the stacks. The red regions in Figure 9 are often buried rather deeply. At the same time, recrystallized areas (blue) are sometimes located above recovered (orange) volumes. This suggests that the microstructure evolution is not merely a function of the number of impacts that have peened a particular volume. Assuming that, to first order, the degree of recrystallization is representative of the degree of deformation and cold work, it follows that there is no simple gradient in degree of cold work from the top to the bottom of the stack, nor is there an obvious "steady-state" deformation condition developed over the duration of the present experiments. If there were a deformation gradient, we would expect to find the sequence red-orange-blue with blue at the bottom (peened the most) and red at the top (not peened at all)—a sequence we do not find. If a steady state had developed the microstructure would be uniform at regions below the near surface. Instead, red and blue portions are not distributed randomly and uniformly throughout the stack but tend to group with their own at certain heights. The process of particle stacking thus clearly involves a stochastic process of freezing local strain concentrations based on nuanced local variations in particle placement,

microstructure, and—perhaps—particle kinetic properties. We turn our attention to this last point in what follows below.

The local variations in microstructure are quantified as modulations of the respective area fractions as a function of stack height (**Figure 9c, g**). **Supplementary Figure 3** describes the analysis in detail. The local area fractions can then be compared to the local particle kinetics in **Figure 9d, h**. Both datasets suggest a spatial correlation between microstructural features and the impact velocity of involved particles. Non-recrystallized volumes (red) seem to be co-located with groups of particles of (mostly) below-average velocity, and fully recrystallized grains (blue) with a number of high-velocity impacts. In particular, all impacts of velocity significantly above average (ca. >370 m s⁻¹) can be connected with recrystallized areas. These qualitative observations are substantiated by negative linear correlations of red area fractions with impact velocity (R=-0.27 and R=-0.22), and stronger, positive correlations of blue area fractions with velocity (R=0.39 and R=0.27) (**Figure 10**). No or only weak correlation was found for the intermediate (orange) stage.



Figure 9. Correlation between microstructures and particle impact parameters. a, e) Cross-sections (BSE SEM, tiltcorrected) of two particle stacks with characteristic microstructures outlined. b, e) Microstructure maps assembled from analysis of four cross-sections per stack. Red areas represent the heavily deformed but original particle microstructure. Blue are areas of stress-free, micrometer-scale grains (the recrystallized microstructure that underwent grain growth). For clarity, orange sections were omitted in these presentations. c, g) Area fractions for each microstructure group as a function of stack height (cumulative particle diameter). d, h) Spectra of velocity and kinetic energy of the individual particles plotted as a function of cumulative particle diameter. The plots are scaled and aligned to the total height of the deposit, as in Figure 7. The microstructure map from (b, f) is overlaid. Both datasets hint towards a spatial correlation between non-recrystallized volumes (red) with groups of particles of (mostly) below-average velocity, and stress-free, microscale grains (blue) with a number of high-velocity impacts.



Figure 10. Linear correlation between local microstructure and local impact velocity. Scatter plots relating the area fractions of the three different microstructures to the local impact velocity: **a-c**), first stack, and **d-f**), second stack from Figure 9. The linear correlation of particle velocity is negative with the fraction of initial, deformed microstructure (red) (R=-0.27 (a) and R=-0.22 (d)); but is positive with recrystallized area fraction (R=0.39 (b) and R=0.27 (e)). No or very weak correlation between local impact velocity and the intermediate microstructure (orange) is found.

That faster impacts lead to more evolution towards recrystallization speaks to an effect of local strain; faster particles (or groups of particles) experience more strain and thus are more poised to recrystallize. Hence, we also attempt an analysis purely based on microstructural data that relates the microstructure evolution to the degree of local deformation. In Figure 11a, the local particle flattening is used as an estimate of local strain, by comparing splat heights along the centerline of the stack. We only measure splat heights instead of the ratio of splat height to width, because detecting the complete outlines of splats was not always possible-especially in areas of recrystallization, the interfaces were obliterated. Because a reasonable agreement between the flattening estimated by splat height and that estimated by splat aspect ratio was found (Supplementary Figure 4), we have used the less precise but more reliable strain estimation only based on splat height. Here, the vertical distance between particle-interfaces is converted to a proportional grayscale value. The sum of the grayscale values from four crosssections can be read as a qualitative 1D strain map that represents local strain as a function of stack height (Figure 11b). In this case, the area with highest strain is located at approximate half height of the stack. Notably, this region of highest strain correlates with the region of most pronounced recrystallization (Figure 11d), and also aligns with the proportional position of a group of high-velocity particles (e).



Figure 11. Strain-dependence of grain growth. a) Tow cross-sectional micrographs (SE SEM, tilt-corrected) of the same deposit, sectioned at two different positions. Purple lines mark detected particle interfaces along the centerline of the deposit (if possible). The bar to the right of the micrographs represents these distances with a proportional gray-scale value. Assuming that the flattening ratio of particles and thus the local strain the material underwent is proportional to this interface-spacing, the bar can be read as a qualitative 1D strain map with the local strain proportional to the local gray-scale value (the darker, the more strain). **b)** Four individual maps extracted from four roughly equidistant cross-sections of the deposit are summed to produce a summative 1D strain-map for the whole volume. **c)** Microstructure map as in Figure 9, aligned to the strain map. **d)** Velocity and spectrum of the individual particles plotted as a function of cumulative particle diameter, overlaid with the strain map from b). The velocity plots are scaled to the total height of the deposit, as in Figure 7. **e)** Corresponding area fractions of initial and recrystallized microstructure. At half-height of the stack, a correlation of highest strain, above-average particle velocities and recrystallized areas with significant grain growth (blue) may be concluded.

In combination, these results suggest that a local increase in impact velocity (ca. 10–20% above average velocity) can result in areas of increased strain that in turn may develop an accumulation of recrystallized volume. These experiments thus support the thought that at least part of the microstructural heterogeneity in cold-spray coatings may be caused by strain differences amongst impacted particles, and not only by strain gradients within particles. This points to an interesting direction for future work.

7. Conclusions

Here we have presented a many-particle LIPIT method that reproducibly stacks gold particles (>20 particles) with different characteristic spectra of impact velocity. We have observed successful build-up of stacks but also their impact-induced fracture. Based on average velocity data, we concluded the existence of a velocity for successful accumulation of a coating that is higher than the critical velocity for adhesion of single particles. Further, we have demonstrated first attempts to correlate individual particle velocity data with internal features of the coating. While not fully conclusive, the data suggests a relationship between local porosity and kinetic energy of particles associated with the porous volume. Finally, a correlation between particle impact velocity, local strain, and recrystallized fraction hints towards an influence of straingradients between particles—and not only within single particles—on the heterogeneous microstructure of cold-spray coatings. We have discussed that a limitation of the presented experiments is the merely proportional instead of absolute relation of the kinetic data of individual particles to particle positions inside the stack. Here, more targeted experiments and better analysis will be needed. Nonetheless, the presented analyses outline what is possible. We believe the here-demonstrated extension of LIPIT from a single-particle technique to a method that utilizes particle streams holds promise for the versatile study of many-particle impact phenomena-enabling a quantitative view of the behavior of individual particles to the study of pore formation, inter-particle fracture, or particle deformation and related microstructure evolution. The experiments could easily be extended to particle counts of 100-1000 if needed. LIPIT has thus potential for experimentally simulating impact-based, manyparticle processes all the way from single-particle impacts to the collective behavior of large

numbers of particles in different domains of microparticle impact—from interaction of particles in cold spray to multi-step erosion processes.

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8. Supplementary Information



Supplementary Figure 1. Pore formation in stack from Figure 7e. A sequence of cross-sections throughout the particle stack document connection between upper and lower portion only through a small portion of material (fourth micrograph). It can be well imagined that such a protrusion—a small particle, or the upward extrusion of material from the particle impact below—that is impacted with larger, low-energy particles (as indicated by the energy spectrum) can result in a large gap as observed. Impacting particles might have sufficient energy to bond to the point of first impact (the protrusion) but not sufficient extra energy to also bond to the larger particles below—they rebound but remain attached to the protrusion that acts as a hinge. It should be noted that no small particle <10 μ m was registered in the LIPIT experiments—it might have been a satellite particle connected to a larger particle.



Supplementary Figure 2. Microstructure of stacks. a, c) The complete set of cross-sections (BSE SEM, tilt-corrected) of the two particle stacks shown in the main text, with characteristic microstructures outlined. **b, e)** Microstructure maps assembled from the analysis of these four cross-sections. Red areas represent the heavily deformed but original particle microstructure. Blue are areas of stress-free, micrometer-scale grains (the recrystallized microstructure that underwent grain growth). For simplicity, the transitional microstructure is only indicated in the first micrograph (Orange).







Supplementary Figure 4. Comparison of local strain measurements. a) Cross-sectional SE SEM micrograph with particle outlines highlighted in the right image. Full particle interfaces cannot always be seen. Here, approximate positions for the interfaces were assumed. **b)** Splats from a) shaded in a greyscale value proportional to the aspect ratio of their bounding box (that is, flattening ratio, proportional to the strain). **c)** 1D strain map from the same cross section, derived as described in the main text (grayscale values are not related to those in b)). Qualitatively, the two analyses are in agreement: highest strain is located in a volume at half height of the stack. Because of the general uncertainty in locating splat outlines as in a), we have used the less precise but more reliable strain estimation as in c).