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# Atomistic investigation on the structure–property relationship during thermal spray nanoparticle impact

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ABSTRACT

During thermal spraying, hot particles impact on a colder substrate. This interaction of crystalline copper nanoparticles and copper substrate is modeled, using MD simulation. The quantitative results of the impacts at different velocities and temperatures are evaluated using a newly defined flattening aspect ratio. This ratio between the maximum diameter after the impact and the height of the splat increases with increasing Reynolds numbers until a critical value is reached. At higher Reynolds numbers the flattening aspect ratio decreases again, as the kinetic energy of the particle leads to increasing substrate temperature and, therefore, decreases the substrate resistance. Thus, the particle penetrates into the substrate and deforms less.



## 1. Introduction

'Thermal spraying' is a standard term used for coating processes where the sprayed layer is first formed by fully or partially melting the material at a high or moderate temperature (e.g. arc, flame, plasma, high-velocity oxy-fuel, detonation spray) or at cold temperature (e.g. cold spray) and then molten/semi-molten droplets are propelled through a spraying gun on the substrate in the form of splats or lamella [1]. Over the years, thermal spraying has gained wide popularity to produce coatings (typically in the thickness range of 50–500 μm) to combat surface degradation of engineered components. Typical industrial examples of thermal spraying include defence, biomedical, marine, nuclear, chemical, automotive, aeronautical and mining [2]. Coating materials such as metals, ceramics and cermets in nanostructured/fine/conventional micron powder sizes are generally used in thermal spray processes. Representative examples include Al/Cu/Ag for electrical components, Cu for printing industries, $Al_2O_3$ for textile and automotive machinery parts, WC-Co based wear-resistant coatings for aero-engine parts, yttria stabilized zirconia (YSZ) based thermal barrier coatings for turbine blades, Ni-based corrosion resistant coatings for chemical reactors and hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ coatings for orthopaedic implants. More recently, thermal spray processes have been used to prepare nanostructured coatings using microsized nanocrystalline powder particles [3].

The properties of coating such as wear resistance, oxidation and corrosion resistance, thermal conductivity, electrical conductivity and self-lubrication are highly dependent on the properties of the splat, which in turn depends largely on spray parameters. A thermal spray is normally carried out using the following steps:

(a) Particles are heated with a flame or an arc at a high temperature in the range of 3000–15,000 °C to melt them.
(b) Molten particles are accelerated in a gas stream (300–3000 m/s) and propelled at high velocity (50–1000 m/s) on the surface to be coated, and
(c) Partially or fully molten particles flatten while impacting the substrate surface (normal or inclined) in the form of disk-like splats or splashes, and subsequently cool down

*Abbreviations:* BCC, body centred cubic; CR, cooling rate; CNA, common neighbour analysis; DXA, dislocation extraction algorithm; *E*, activation energy; *Exx*, strain tensor in *x*, *y* and *z* direction; EAM, embedded-atom-method; FCC, face centred cubic; HCP, hexagonally close packed; HPPT, high pressure phase transformation; *K*, Sommerfeld parameter; LAMMPS, large-scale atomic/molecular massively parallel simulator; MD, molecular dynamics; NVE, micro-canonical ensemble; NVT, canonical ensemble; OVITO, open visualization tool; *R*, universal gas constant; Re, Reynolds number; $\mu_0$, viscosity at the melting point; VMD, visual molecular dynamics; We, Weber number; YSZ, yttria stabilized zirconia.

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(typically at 100–600 K/μs) and coalesce to yield the desired coating. In general, Sommerfeld parameter $K$ ($K = We^{1/2}\,Re^{1/4}$ where We and Re are Weber number and Reynolds number respectively) is used to study the behaviour of the splat [4]. Without solidification on a dry surface, Sommerfeld parameter characterizes the droplet behaviour as follows [5]: $K < 3 \rightarrow$ rebound, $3 < K < 57.7 \rightarrow$ deposition, $K > 57.7 \rightarrow$ splashing.

While thermal spray processes for single particle elastic impacts provide some insights, the problem becomes complex when spraying involves a multitude of particles undergoing significant plastic deformation and fragmentation due to a number of simultaneously occurring processes such as the collapse of particle agglomerations, phase changes, adhesion and metallurgical transformations [6].

Macroscopic properties of thermal spray coatings such as hardness, porosity, surface roughness and mechanical strength depend on their microstructure. Previous studies have highlighted that the substrate's temperature with respect to Leidenfrost temperature influences the tribology between the liquid droplet and the substrate [5]. Overall, while research in the arena of thermal spray is progressing [7], there are still many unexplored areas which may lead to improvements in this technology. Apart from experimental approaches to study thermal sprays [8], modelling approaches are also evident in the literature i.e., computational fluid dynamics [9], Monte-Carlo simulation [10], smooth-particle hydrodynamics [11] and finite-element methods [12] have been applied to study thermal spraying processes. Analytical models of droplet solidification on flat surface have also been proposed, but they are only able to explain the phenomena for a limited range of materials/conditions [13,14]. Moreover, recent trends in thermally sprayed ceramic coatings show a shifted emphasis on producing coatings with nanostructures or finer microstructures [15], in order to make use of the potential properties of the thick coating materials. Thus, there is a need to understand surfaces, interlayers and interfaces at an atomistic level in the thermal spray process. Since the relationship among processing conditions, particle characteristics, and the resulting coating properties is highly nonlinear and might not be thoroughly revealed by experimental studies, atomistic modelling can play an important role in the design and operation of thermal spray processes. An accurate understanding of thermal spray coating requires an insight into the structural, dynamic, energetic and rheological aspects in an atomic framework rather than the continuum framework [16,17]. Advances in modern computation and extant literature in the field of solid particle impact mechanisms also indicate that atomistic modelling is an excellent approach to complement the experimental findings. Such modelling can provide a better understanding of the underlying momentum, heat-transfer and other important mechanisms, which in turn, may be used to guide parameter design of thermal spray processes. Moreover, understanding the variability of a thermal spray process in real-time is essential to fabricate coatings having deterministic finish. Molecular dynamics (MD) simulation is an intermediate tool to bridge the gap of first principles, macroscopic and finite element methods, and is the method of choice when the properties to be studied are observable within the time scale accessible to simulations.

Since MD provides higher temporal and spatial resolution and capability to examine a phenomenon within a range of few picoseconds to femtoseconds; it is an appropriate choice for this work. The pioneering work of Shimizu et al. [18] is the only reported MD work in this domain to the best of authors' knowledge. Shimizu et al. [18] developed the models of aluminium–aluminium spray system using simple approximations of the Morse potential function. Their work does not take into account the resulting topography of the splat below the substrate's surface which can also affect the flattening process. In contrast to their work, the current work reports results for a copper–copper system described by a relatively better potential energy function. Some of the key questions that are addressed through this paper are:

(a) In a copper–copper thermal spray system, does the flattening aspect ratio vary with Reynolds number? Which other factors affect the flattening aspect ratio?
(b) What is the relative importance of the impact velocity and the temperature of the impacting particles in influencing the deviatoric strain energy induced in the substrate?
(c) How do the intermetallic properties vary with the change in temperature and velocity of the impacting particles?
(d) What are the time scales involved in flattening and solidification of the splat?

The above questions motivate the development and implementation of MD simulations in the current work. Exploration and analysis of parameters affecting the microstructure of coatings (e.g. which factors affect stress distribution) [19,20], will help enhance understanding of the thermal spray processes.

## 2. MD simulation

In this work, the "Large-scale atomic/molecular massively parallel simulator" (LAMMPS) [30] was used to perform a series of MD simulations. VMD [31], OVITO [32], and the dislocation extraction algorithm (DXA) [21–23] were used to visualize and analyze the atomistic simulation data. The following paragraphs detail the model and the algorithm followed in this work.

### 2.1. MD simulation model

A schematic diagram of the thermal spray MD simulation model is shown in Fig. 1. Periodic boundary conditions were applied in both $X$ and $Z$ axes of the system. The atoms of the substrate were allocated into one of the three different zones: Newton atoms, thermostatic atoms and boundary atoms, while the impacting particles were allocated to the zone of Newton atoms. The boundary atoms were assumed to be fixed in their initial lattice positions, serving to reduce the boundary effects and maintain the symmetry of the lattice. Newton atoms were allowed to follow Newtonian dynamics (LAMMPS NVE dynamics), while atoms in an intermediate thin boundary layer were subjected to a thermostat (LAMMPS NVT dynamics) to dissipate the extra heat generated in the finite simulation volume. This consideration of boundary conditions ensures that the process of deformation is not affected by any artificial dynamics. It may be noted here that this work considers vacuum which although an unpractical consideration, is still a good assumption to discard the role of ambient air or gas in order to make a careful examination of the effect of droplet momentum and the consequent splat formation.

### 2.2. MD simulation inputs

There are two significant phenomena involved in a thermal spraying experiment in general [2]:

1. If the sprayed particle temperature is lower than (but close to) the melting temperature, a high impact velocity is sought.
2. At temperatures above the melting point, the viscosity of the liquid particle decreases significantly. The viscosity $\mu$ follows the relationship $\mu = \mu_0 \cdot \exp(E/RT)$ where $E$ is activation energy and $\mu_0$ is the viscosity at the melting point. Hence, a relatively lower velocity is needed.