MD Simulation on Collision Behavior Between Nano-Scale TiO₂ Particles During Vacuum Cold Spraying

Hai-Long Yao¹, Guan-Jun Yang²*, and Chang-Jiu Li²

¹Jiangxi Province Engineering Research Center of Materials Surface Enhancing and Remanufacturing, School of Mechanical and Materials Engineering, Jiujiang University, Jiangxi, 332005, China
²State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi’an Jiaotong University, Xi’an, 710049, China

Particle collision behavior influences significantly inter-nano particle bonding formation during the nano-ceramic coating deposition by vacuum cold spraying (or aerosol deposition method). In order to illuminate the collision behavior between nano-scale ceramic particles, molecular dynamic simulation was applied to explore impact process between nano-scale TiO₂ particles through controlling impact velocities. Results show that the recoil efficiency of the nano-scale TiO₂ particle is decreased with the increase of the impact velocity. Nano-scale TiO₂ particle exhibits localized plastic deformation during collision at low velocities, while it is intensively deformed by collision at high velocities. This intensive deformation promotes the nano-particle adhesion rather than rebounding off. A relationship between the adhesion energy and the rebound energy is established for the bonding formation of the nano-scale TiO₂ particle. The adhesion energy required to the bonding formation between nano-scale ceramic particles can be produced by high velocity collision.

Keywords: MD Simulation, Collision Behavior, TiO₂, Vacuum Cold Spraying, Particle Bonding.

1. INTRODUCTION

Nano-ceramic coatings have attracted intensive scientific interest due to their potential applications in diverse fields such as catalysis, optics, energy, membranes, and biomedicine.¹-⁴ Vacuum cold spraying (or aerosol deposition) is a promising coating process to deposit ceramic and temperature-sensitive materials due to its merit of low-temperature during the deposition process.¹-⁵ In this approach, particles of ceramic materials with a diameter of being less than 1 μm are accelerated to a velocity of 100–600 m/s to impact on a substrate or deposited particles to form a coating. During spraying, the coating deposition depends on not only collisions between particles and the original substrate, but also collisions between impacting particles and deposited particles which serve as the in-situ substrate.⁶ It was reported that materials with good inter-particles connection have higher mechanical and electric properties than their counterparts with poor inter-particle connection.⁷-¹⁰ Therefore, inter-particle bonding formation plays an important role in determining the properties of particle-deposited materials.

Particle bonding depends on collision behavior of the particles for solid particle deposition processes. For metallic materials, mechanisms of particle bonding and deposition in cold spraying are widely studied and relatively well understood.¹¹-¹³ A main point in cold spraying is that metallic particles deposition takes place essentially via intensive plastic deformation due to adiabatic shear instability at the interacting surfaces. However, ceramic materials are completely different from the ductile metallic materials due to their obvious brittle behavior.

Based on the cross-sectional microstructure observation of vacuum cold sprayed ceramic materials using sub-micro-sized particles, the fine particle compaction following the starting particle fragmentation is assumed as the main reason for sub-micrometer ceramic particle deposition.¹,⁶ Most experimental results showed that sub-micrometer ceramic particles can be broken into fragments by high velocity collision.¹,⁵,⁶,¹⁴ Simulation results further showed that the fine particle fractures during high velocity impact.¹⁵ On the contrary, some other studies argued that, despite the induced brittleness, ceramic particles start to deform without breaking into fragments, as the particle size falls below a critical value.¹⁶,¹⁷
In addition to single sub-micron ceramic particle deposition, agglomerates of nano-scale ceramic particles are also deposited by vacuum cold spraying to form porous coatings.\textsuperscript{18,19} The investigations showed that near-spherical agglomerates can be deformed to hill-like variations due to the high pressure resulting from the high velocity impact during vacuum cold spraying.\textsuperscript{20,21} Although some results obtained by MD simulation exhibit fragmentations of ceramic particles by high velocity collision,\textsuperscript{15} there is no experimental result about particle fragmentation for nano-scale ceramic particles during depositing agglomerates.\textsuperscript{18–21} The results obtained by HRTEM examination confirm that no particle fragmentation is found when nano-scale particles deposited onto the substrate by vacuum cold spraying.\textsuperscript{22} Those phenomena imply that the particle fragmentation may be not the main reason for nano-scale ceramic particles bonding and deposition. By analyzing the deposition process, collision mainly occurs between nano-scale ceramic particles during the deposition of agglomeration. Therefore, it is necessary to illuminate the collision behavior between nano-scale ceramic particles by high velocity collision.

In this study, collision behavior between nano-scale TiO\textsubscript{2} particles was explored by the method of molecular dynamic simulation. The effects of impact velocity on temperature, microstructure change and bonding state of nano-scale TiO\textsubscript{2} particle were illuminated. Furthermore, particle bonding formation was discussed from the point of view of the competition between the adhesion energy and rebound energy.

\section*{2. METHODS}

According to the particle deposition process during vacuum cold spraying,\textsuperscript{1} a model of a moving particle colliding onto a fixed particle was applied in this study. Molecular dynamics simulation was employed to investigate the collision behavior between the nano-scale TiO\textsubscript{2} particles. Buckingham-type potential proposed by Matusi and Akaogi is used here as it reproduces best the TiO\textsubscript{2} crystal structure of rutile, anatase, and brookite.\textsuperscript{23} This atomistic force field can be rewritten in a site–site interaction form.\textsuperscript{23,24}

\[ U(r_{ij}) = A_{ij} \exp \left( \frac{r_{ij}}{\rho_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6} q_i q_j \]  

where \( U(r_{ij}) \) is the interaction energy between sites \( i \) and \( j \) and the parameters \( A_{ij}, \rho_{ij}, \) and \( C_{ij} \) are listed in Table 1. The charges \( q_i \) for titanium and oxygen are +2.196 and -1.098, respectively, in atomic units.

Molecular dynamics simulations have been carried out with the molecular dynamic code Lammps. Perfect lattices of these phases were prepared by using the experimental lattice parameters.\textsuperscript{23,24} In this study, two spherical particles with a diameter of 3.8 nm are cut out from a perfect anatase TiO\textsubscript{2} crystal, as shown in Figure 1. Conventionally, molecular dynamic simulation focus on atom behavior. However, temperature is a statistical average parameter of a certain amount of atoms’ energy. Therefore, the fixed particle is divided into three parts in order to make sure that each part is composed of a certain amount of atoms and thereby to estimate the surface temperature of the particle, i.e., the temperature of impact interface. In this study, the fixed particle is divided into three parts at the impact direction: bottom fixed layer consisting of 4 layers, middle constant temperature layer consisting of 11 layers and surface free layer consisting of 6 layers. Periodic boundary conditions were not used and all atom–atom interactions were directly included in the simulation by ensuring that the cutoffs for the force and energy calculations were greater than the diameter of the nanoparticles in all simulations by 10 Å. Before collision, the moving particle and fixed particle are equilibrated at 300 K by temperature rescaling for 40 ps with a time step of 0.5 fs.\textsuperscript{23,24} Then, the quantity of equilibration and energy conservation are tested by integration in the micro-canonical ensemble (NVE) for additional 10 ps. See Figure 1 for snapshots of TiO\textsubscript{2} particles configuration before and after equilibration.

\begin{table}[h]
\centering
\caption{Interaction parameters for Eq. (1),\textsuperscript{23,24}}
\begin{tabular}{llll}
\hline
Interaction & \( A_{ij} \) (kcal mol\textsuperscript{-1}) & \( \rho_{ij} \) (Å) & \( C_{ij} \) (kcal mol\textsuperscript{-1} Å\textsuperscript{-6}) \\
\hline
Ti–Ti & 717654 & 0.154 & 120.997 \\
Ti–O & 391053 & 0.194 & 290.392 \\
O–O & 271719 & 0.234 & 696.941 \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Snapshots of TiO\textsubscript{2} particles configuration before and after equilibration. (a) Before, (b) after. (In fixed particle, atoms of Ti an O are colored as red and blue respectively. In moving particle, atoms of Ti an O are colored as dark blue and yellow respectively.)}
\end{figure}
During collision process, the middle layer of the fixed particle is maintained at 300 K by scaling the velocity of constituting atoms. The temperature of surface free layer of the fixed particle as well as the moving particle is not controlled in order to study the balance of energy during the collision process. The simulation is performed with a minimum separation of 2 nm between the closest boundaries of both the particles. Collision simulations are carried out for 30 ps in the micro-canonical ensemble (NVE) under the initial particle temperature of 300 K. Collision behaviors of the particles were illuminated by controlling initial impact velocities of the moving particle (150 m/s, 300 m/s, 600 m/s, and 1200 m/s). Simulation was implemented on the platform of Intel cores with Linux operation system.

3. RESULTS AND DISCUSSION

3.1. Temperature and Trajectory of Particles During Collision

Figure 2(a) shows the effect of initial impact velocity on the temperature of the surface free layer in the fixed particle. It can be found that the temperature of the surface free layer increases with the impact velocity. Meanwhile, the temperature of the moving particle also increases with the increase of the initial velocity as shown in Figure 2(c). The maximum temperature of both the moving particle (Fig. 2(d)) and the surface free layer of fixed particle (Fig. 2(b)) is much less than the melting temperature of anantase-TiO2 at present velocities. Due to existence of the constant temperature layer, the temperature of both the fixed particle and the moving particle decreases, and trends to the initial temperature of the fixed particle. This phenomenon clearly reveals that the nano-scale TiO2 particles always remain solid state during collision.

Figure 3(a) shows a typical velocity trajectory of the moving TiO2 particle colliding onto the fixed TiO2 particle. Since the impact-direction (perpendicular to the surface of the fixed particle) points from the moving particle to the fixed particle, the moving particle has a positive velocity initially. The magnitude of the final velocity of the moving particle decreases and decays to around zero, indicating that the kinetic energy is lost by interactions between the moving particle and the fixed particle. This simulation continues for a total time of about 30 ps, and a separation between the moving particle and the fixed particle is never observed over the course of simulation (as shown in Fig. 3(a)). This phenomenon indicates that the moving particle is bonded together with the fixed particle. Comparing the change of moving particle velocity (Fig. 3(a)) and the particle temperature (Fig. 2) with the impact time, it indicates that the lost of kinetic energy is not completely transferred to the thermal energy. If all the lost kinetic energy is converted to the thermal energy, the
temperature increase will be linearly proportional to the square of impact velocity, since the kinetic energy is in linear proportion to the square of impact velocity. This result indicates that some of the lost kinetic energy has to be transferred to fracture energy, which is further elucidated later in this section.

Figure 3(b) shows the impact time and contact time between the moving particle and the fixed particle. As described in literature, the impact time refers to the time span in which the particle velocity decreases from the initial velocity to the first zero, and the contact time refers to the time span in which the velocity of moving particle decreases from its initial velocity to the negative maximum velocity. It can be found that both the impact time and contact time overall increase with the increase of the impact velocity and then tend to a constant value except the occurrence of an extreme value at an impact of 300 m/s. Therefore, the evolution of both the impact time and contact time undergo a quite complex tendency which needs further exploration later in the following section.

Furthermore, a recoil velocity of the moving particle can be obtained according to the trajectory. The recoil efficiency \( e_r \) refers to the a maximum inverted velocity of the moving particle according to the velocity trajectories,

\[
e_r = \left( \frac{V_{\text{recoil}}}{V_{\text{impact}}} \right)^2
\]
bonded together for the cases in this study. This results clearly proved the bonding between two particles shown in Figure 3(a) in the last section. In addition, the diameter of bonding neck between particles is increased with the increase of the initial velocity, and amount of atoms displacing from equilibrium positions (around the compacting zone) is also increased. As the initial impact velocity being less than 600 m/s, only those atoms near the compact region displace from the equilibrium positions (within a few atomic spacing), while atoms far from the compact region are immobile (beyond a few atomic spacing). This phenomenon indicates that the nano-scale ceramic particle exhibits localized plastic deformation (or ductile) by collision even at low velocities. Those simulation results for low velocities are consistent with the experimental results that particle fragments cannot be found during depositing agglomerates by vacuum cold spraying.\(^1\)\(^{,}\)\(^{21}\)

To quantitatively analyze particle bonding states, a contact area ratio was defined in this study as the following expression:

\[
\text{Contact area ratio} = \frac{r}{R}^2
\]  

where \(r\) refers to the particle neck diameter, and \(R\) refers to the particle diameter.

It can be found from Figure 4 that the nano-scale particle still exhibits no obvious fragments, although it can be intensively deformed by collision at high velocities. Therefore, it is necessary to illuminate the condition of particle fracture. According to descriptions in literature,\(^27\) thermodynamic considerations have led to the following fracture energy equation:

\[
E_F = 4.2K_{IC}^2V_{\text{impact}}\frac{1/d_i - 1/d_0}{E}
\]

where \(K_{IC}\) is the critical stress intensity factor or fracture toughness. This parameter deals with the fracture resistance of the material and is a measure of the critical stress (or strain energy) level for crack propagation. \(V_{\text{impact}}\) is the impact velocity of particle. \(E\) is the elastic modulus of the material, and \(d_i\) and \(d_0\) are the final and initial grain size, respectively.

Figure 6 shows the fracture energy and kinetic energy of the TiO\(_2\) particle. Conventional considerations are that the ceramic particle fracture occurs as the kinetic energy is higher than the fracture (fragment) energy.\(^27\) However, the kinetic energy of the nano-scale TiO\(_2\) particle is still less than the fracture energy at present velocities (considering the 3.8 nm particle crushed into small fragments, for example 1.9 nm or 0.95 nm particles as shown in the

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**Figure 4.** Snapshots of bonded particles for different initial impact velocities. (In fixed particle, atoms of Ti and O are colored as red and blue respectively. In moving particle, atoms of Ti and O are colored as dark blue and yellow respectively).

**Figure 5.** Effect of initial impact velocity on contact area ratio of bonded particles. (a) Schematic diagram of particle bonding ratio; (b) contact area ratio.
inset table in Fig. 6). Therefore, the nano-scale particle still exhibits no obvious fragment as shown in Figure 4. This phenomenon indicates that the nano-scale ceramic materials can be even intensively deformed, and do not present any fragment. This could be attributed to that the nano-scale ceramic particle exhibits ductility and atoms in those nano-scale particles exhibit a high migration ratio due to their high specific surface area.

3.3. Relationship Between the Adhesion

Energy and Rebound Energy

For solid particle deposition approach, the coating deposition is the result of competition between particle rebound and particle bonding. Due to the competition of the adhesion energy and rebound energy, particle bonding can be affected by the impact conditions (temperature and velocity) and the material properties of the feedstock and substrate.\textsuperscript{15} For cold spraying, the relationship between the metallic particle rebound and bond has been well studied.\textsuperscript{11} However, this relationship for ceramic particle of vacuum cold spray has never been reported. Although ceramic materials are always brittle, nano-scale ceramic materials are regarded as ductile\textsuperscript{28–30} and also be proved by the results obtained in this study. This implies that theories for the rebound energy and adhesion energy based on metallic particles might be partly favor to analyze the nano-scale ceramic particles. Therefore, the relationship between the rebound energy and adhesion energy is discussed in this study to explain the bonding phenomenon of nano-scale TiO\textsubscript{2} particles.

As described in literature,\textsuperscript{11} the energy required for bouncing the particle from the substrate during the unload moment is defined as the rebound energy in the impact process of kinetic spraying. According to the drop-ball dynamic hardness test,\textsuperscript{32,33} the rebound energy \((R)\) can be expressed as:

\[
R = \frac{1}{2} m_p V_{\text{impact}}^2
\]

where, \(m_p\) is the particle mass.

Correspondingly, the process of adhesion interaction is regarded as one of bonding generation between the particles during contact. According to the solution of the kinetic equation of the interaction between atoms at the phase boundary, Shorshorov and Khramlov developed a relation for the relative strength of the bond between the particles and the substrate.\textsuperscript{34} Kurochkin et al. improved this relation by taking the velocity contribution in the interaction of the particles and the substrate into account.\textsuperscript{26} Therefore, the relative bonding strength with allowance for the “velocity” contribution to the energetic of the interaction between the deformed particles and the substrate is determined from the formula:

\[
\alpha = 1 - \exp\left(-\nu t_c \exp\left[\frac{-E_a}{kT_c + (1 - e_r) m_p V_{\text{impact}}^2/2}\right]\right)
\]

where \(\nu\) is the natural frequency of the atoms, \(E_a\) is the activation energy of the chemical bonds, \(T_c\) is the temperature in the contact zone, \(k\) is the Boltzmann constant, \(t_c\) is the particle-substrate interaction time, \(m_p = M_p/NA\), \(M_p\) is the atomic mass of the particle materials, and \(N_A\) is the Avogadro number. The adhesion energy \((A)\), which is defined as the energy for detaching the bonded particle from other particle, is expressed as:

\[
A = a A_{\text{max}}
\]

where \(A_{\text{max}}\) is the maximum adhesion energy of a given particle to the substrate particle, \(a\) is the fraction of bonded atoms per unit adhesion interface, and is also called the relative strength of the bond between the particle and substrate.

In addition, the adhesion energy not only can be estimated by using the Eq. (7), it can also be estimated by measuring the total energy of the simulation system. Therefore, the adhesion energy is also estimated as the following expression:\textsuperscript{35,36}

Adhesion energy

\[
= (\text{TotEng}(A) + \text{TotEng}(B)) - \text{TotEng}(AB)
\]

where the \(\text{TotEng}(A)\) is the sum of potential energy and kinetic energy for particle A, the \(\text{TotEng}(B)\) is the sum of potential energy and kinetic energy for particle B, and the \(\text{TotEng}(AB)\) is the sum of potential energy and kinetic energy for the bonded particle (AB).

Figure 7 shows the rebound energy of nano-scale ceramic particles derived by high velocity collision. It can be found that when the impact velocity is less than 600 m/s, the rebound energy increases. While the impact velocity is larger than 600 m/s, the rebound energy decreases. This phenomenon for the rebound energy of ceramic particles is different from that of metallic particles reported in literature.\textsuperscript{31} It was reported that the metallic particle presents intensive plastic deformation,\textsuperscript{11,13} and the
Compared to Eq. (7), the results obtained by Eq. (8) reasonably understand the impact behavior of ceramic particles without fragmentations. In contrast, atoms in ceramic particles are intensively displaced from their equivalent sites by high velocity collision, thereby “rebound energy” cannot be recovered in the ceramic particle.

Particles bonding forms at the condition that the adhesion energy is higher than the rebound energy. Particle fragmentation is usually regarded as the main reason for bonding formation of sub-micron ceramic particles. While bonding formation between nano-scale ceramic particles without fragments is seldom mentioned. Figure 7 shows the adhesion energy between nano-scale particles derived by high velocity collision. It can be found that when the impact velocities is larger than 600 m/s, the adhesion energy is obviously higher than the rebound energy. This result indicates the bonding formation can be realized between the nano-scale ceramic particles. Results obtained by MD simulation show nano-scale ceramic particles are intensively deformed by collision at high velocities, and confirm the particles bonding formation as shown in Figure 4(d). As the initial velocity being less than 600 m/s, the adhesion energy obtained by Eq. (8) is closed to the rebound energy. The adhesion energy obtained by Eq. (7) was less than the rebound energy and thereby indicated no bonding between nano ceramic particles. However, this theoretical prediction is not consistent with the experimental data in this study. Therefore, Eq. (7) of the adhesion energy developed for metallic particles is not suitable for nano-scale ceramic particles most possibly due to the intrinsic difference of deformation between metallic and ceramic particles. In order to comprehensively understand the impact behavior of ceramic particles, then we introduce Eq. (8) to estimate the adhesion energy in terms of atoms bonds regardless of materials properties, which is widely applied during MD simulation. Compared to Eq. (7), the results obtained by Eq. (8) reasonably explain the nano-scale ceramic particles bonding phenomena. Thus Eq. (8) for adhesion energy is suitable for nano-scale ceramic particles. Microstructural results showed that ceramic particles usually exhibit localized plastic deformation, and also confirm the particles bonding formation as shown in Figures 4(a)–(c). Those simulation results are consistent with the experimental results that nano-scale ceramic particles are bonded together without obvious fragmentations. This phenomenon indicates that bonding formation between nano-scale ceramic particles can be realized by localized deformation without obvious fragments.

4. CONCLUSIONS
Molecular dynamic simulation was applied to explore the impact process between nano-scale TiO_2 particles through controlling impact velocities. The recoil coefficient of the nano-scale TiO_2 particle was decreased with the increase of the impact velocity. Simulation results showed that only those atoms near the compact region displaced from the equilibrium position at low velocities; while particles were intensively deformed by collision at high velocities. Result obtained by MD simulation indicates that the nano-scale ceramic materials can be even intensively deformed without any fragment. A relationship between the adhesion energy and the rebound energy was built for nano-scale TiO_2 particles. Results show that the adhesion energy required to the bonding formation for nano-scale ceramic particles can be produced by high velocity collision.

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References and Notes

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