Effect of Particle Size and Impact Velocity on Collision Behaviors Between Nano-Scale TiN Particles: MD Simulation

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Inter-particle bonding formation which determines qualities of nano-scale ceramic coatings is influenced by particle collision behaviors during high velocity collision processes. In this study, collision behaviors between nano-scale TiN particles with different diameters were illuminated by using Molecular Dynamics simulation through controlling impact velocities. Results show that nano-scale TiN particles exhibit three states depending on particle sizes and impact velocities, i.e., bonding, bonding with localized fracturing, and rebounding. These TiN particles states are summarized into a parameter selection map providing an overview of the conditions in terms of particle sizes and velocities. Microstructure results show that localized atoms displacement and partial fracture around the impact region are main reasons for bonding formation of nano-scale ceramic particles, which shows differences from conventional particles refining and amorphization. A relationship between the adhesion energy and the rebound energy is established to understand bonding formation mechanism for nano-scale TiN particle collision. Results show that the energy relationship is depended on the particle sizes and impact velocities, and nano-scale ceramic particles can be bonded together as the adhesion energy being higher than the rebound energy.

Keywords: MD Simulation, Collision Behavior, TiN, Vacuum Cold Spraying, Particle Bonding, Adhesion Energy.

1. INTRODUCTION

With the development of nanotechnology, there has been a tremendous growth in the application of nanoparticles (NPs) for drug delivery systems, antibacterial materials, cosmetics, sunscreens, and electronics.1-4 Nanoparticles generally possess dramatically different physicochemical properties compared to fine particles (FPs) of the same composition. The smaller size of NPs ensures that a large portion of atoms will be on the particle surface. Since surface properties, NPs are currently of intense interest due to their size dependent magnetic, optical, electronic, and catalytic properties.5-8

Titanium nitride (TiN) is best known for its merits such as good wear and corrosion resistance, biocompatible and electrical properties, which is widely applied to the fields, such as cutting tools9 and biomedical implants.10,11

Titanium nitride coatings can be obtained by using various methods, such as laser,12 reactive plasma spraying,13,14 PVD (Physical Vapor Deposition) and CVD (Chemical Vapor Deposition).15 Although those methods can prepare TiN coatings with high qualities, there are still some disadvantages, such as a high cost, a low deposition rate and a high deposition temperature. Therefore, the development of methods to prepare TiN coatings with a low temperature and a high deposition rate is still the most studied issue.

High velocity collision process is considered to be a substantial technique to prepare TiN coatings. Due to its merits of low-temperature, low-cost, and easy operation,16, 17 high velocity collision process has garnered worldwide attentions for its realistic applications in diverse fields, such as energy,18 optics,19 and biomedical.20 Recently, some researchers have applied this process to deposit TiN coatings.21-23 Results show that vacuum-cold sprayed TiN coatings exhibit excellent mechanical and
During vacuum cold spraying, the main reason for the deposition of ceramic coatings is considered to be plastic deformation (i.e., amorphization, rotated grain, slip bands, and distorted lattices in the transition structure). That phenomenon revealed elastic-to-inelastic transitions of TiN particles at a high strain rate and a high pressure induced by high-velocity impact. In order to properly control qualities of the vacuum-cold sprayed TiN coatings, particles depositing processes is necessary to be understood. Due to limits of high velocities for flying particles and ultra-fine sizes, there is still a challenge to explore impact processes of the TiN particles using experimental methods rather than numerical methods.

Impact behaviors of ceramic particles have been explored by using numerical simulation methods from the point view of particle sizes, velocities and orientations. Simulation results exhibit that the particle fragment is a main reason for the deposition of ceramic coatings. This opinion is confirmed by the microstructure of the sub-micron ceramic particles after impacting, which show refining and fragments of ceramic particles. However, deposition behaviors for agglomerates of nano-scale ceramic particles are different from that for sub-micron ceramic particles. It is reported that although the nano-scale ceramic particle can impact to form coatings, no particle fragments can be observed. According to literature, most experimental studies about the particles refining and fragments after impacting refer to those sub-micron or micron sized ceramic particles rather than particles less than 50 nm or especially ultra-fine sizes. This phenomenon implies that collision behaviors of nano-scale ceramic particles are unclear and may show different phenomena from that of large sized particles.

Furthermore, bonding formations are results of competitions between the rebound energy and adhesion energy of particles during impacting. Recently, relationships between the adhesion energy and the rebound energy for metallic particles collisions are well understood and relative theories are proposed. However, no similar relationships for nano-scale ceramic particles collisions have been reported. Therefore, studying this relationship is beneficial for further understanding bonding mechanism of nano-scale ceramic particles.

In this study, impact processes between nano-scale TiN particles were explored by Molecular Dynamics simulation. Effects of particle size and impact velocity on recoil efficiency, fracture energy and bonding states of nano-scale TiN particle after collisions were illuminated. Furthermore, particle bonding formations were discussed from the point view of the relationship between the adhesion energy and the rebound energy.

2. METHOD

During vacuum cold spraying, flying particles usually impact onto the substrate and deposited particles in order to form coating. Therefore, a model of a moving TiN particle impacting onto a fixed TiN particle was applied in this study as shown in Figure 1. A modified embedded-atom method (MEAM) interatomic potential was applied to investigate atom interactions in TiN particles. Potential parameters were determined by fitting to experimental data on the enthalpy of formation, lattice parameter, elastic constants, thermal linear expansion of NaCl-type TiN, and dilute heat of solution of nitrogen atoms in hexagonal close-packed Ti. This potential can describe fundamental physical properties (structural, elastic, thermal and surface properties) of the alloys well, in good agreement with experimental information or first-principles calculations.

Two spherical TiN particles with the same size were cut out from perfect TiN crystals. 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. According to the experimental process that particles impacting onto the deposited particles, the fixed particle is divided into three parts at the impact-direction: fixed layer (FL), middle constant temperature layer (ML) and surface free layer (SFL) as shown in Figure 1. The simulation is performed with a minimum separation of 4 nm between the closest boundaries of the moving particle and the fixed particle before collision. Periodic boundary conditions were not used to set up MD simulation and all 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, both two TiN particles with centroid velocities of zero were equilibrated at 300 K by temperature rescaling for 50 ps with a time step of 0.5 fs in order to obtain equilibrium states. During collision process, the ML is maintained at 300 K by scaling velocities of constituting atoms. The SFL temperature as well as the moving particle is not controlled.

Then, the quality of equilibration and energy conservation were tested by integration in the micro-canonical ensemble.
(NVE) for additional 20 ps. Collision simulations were carried out for 50 ps in the micro-canonical ensemble (NVE) under the initial particles temperature of 300 K. In order to investigate the effect of particle sizes on collision behaviors, TiN particles with different sizes were applied, e.g., 5 nm, 10 nm and 15 nm. Collision behaviors were also illuminated by controlling initial impact velocities of the moving particle (75 m/s, 150 m/s, 300 m/s, 450 m/s, 600 m/s, 900 m/s, 1200 m/s and 1500 m/s). Incident impacting velocities larger than 600 m/s were unrealistic in the actual deposition\cite{16,17,27} but were adopted in order to simulate high-energy impact cases corresponding to large sized particles. Simulation was implemented by using free open source software of Lammmps on the platform of Intel cores with Linux operation system.

3. RESULTS AND DISCUSSION

3.1. Particle Microstructure and Bonding States Induced by Collision

Through analyzing the snapshots of TiN particles after collision under different conditions, three different states of the nano-scale TiN particles can be observed as shown in Figure 2, i.e., bonding, bonding with localized fracturing, and rebounding. For the bonding state, only those atoms near the impact region around particles boundary significantly displace from their equilibrium positions, while atoms far from the impact region are almost immobility (as shown in Fig. 2(a)). This result indicates that the nano-scale ceramic particles show localized plastic deformations at low velocities. For the bonding with localized fracturing state, both particles exhibit significant deformations due to their high velocity collisions. The near impact regions for both particles are partially fractured and atoms significantly displace from their equilibrium positions (as shown in Fig. 2(b)). In contrast to previous states, the rebounding state exhibits separated particles and partial atoms near impact regions are attached onto the surface of another particle (as shown in Fig. 2(c)), although obvious deformations can be induced by high velocity collisions.

Figure 3 shows a particle map for nano-scale TiN particle states with different sizes and impact velocities. It can be found that TiN particles with a small diameter of 5 nm can be bonded together regardless of initial impact velocities. Merely, particles exhibit localized fracturing at ultra-high impact velocities. As TiN particle sizes up to 10 nm or 15 nm, particles show three different states. TiN particles can be bonded together at low or ultra-high velocities due to localized atoms displacements or localized fracturing, and can also be rebounded at medium velocities. For ceramic particle depositions during high velocity impact process, the impact velocity is usually less than 600 m/s. Incident velocities larger than 600 m/s are unrealistic in the actual process but were adopted in order to illuminate high-energy impact cases corresponding to large sized particles. Furthermore, these simulation results are consistence with the experimental results of depositing nano-scaled agglomerates\cite{29–31 }and sub-micron particles.\cite{16,21–23}

3.2. Fracture Energy of the Nano-Scale TiN Particles

It can be found that partial fractures around the impact regions of the nano-scale TiN particles can be widely found as increasing initial impact velocities. It was reported that particle fragments need enough fracture energies.\cite{35} Therefore, the fracture energy of the nano-scale TiN particle collision should be taken into account. According to literature,\cite{35} thermodynamic considerations have led to the following fracture energy equation:

$$E_F = 4.2K_{IC}^{2}V_{impact}\frac{1/d_i - 1/d_0}{E}$$  \hspace{1cm} (1)

$K_{IC}$ is a critical stress intensity factor. 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. $V_{impact}$ is the initial impact velocity of nano-scale
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Figure 3. Summarized map for TiN particle bonding states.

Figure 4. Fracture energy and kinetic energy of the nano-scale TiN particle.

3.3. Relationship Between the Adhesion Energy and Rebound Energy

For solid particle collision processes, the particle bonding formation is considered as results of competitions between the rebound energy and the adhesion energy. It is reported that particle bonding formation depends on the impact conditions (size and velocity) and the material properties of both the feedstock and the substrate.\(^{16, 24, 29, 30}\) The relationship between the metallic particles rebound and bond has been well studied. However, similar relationships for ceramic particle of vacuum cold spray have never been reported. Therefore, the relationship between the rebound energy and adhesion energy should be discussed to understand the nano-scale TiN particle bonding phenomenon. In this study, we only considered effects of size and velocity on particle bonding formation during collision.

It was reported that the energy required for bouncing the particle from the substrate during the unloading moment is defined as the rebound energy in the impact process of kinetic spraying.\(^{36, 37}\) According to the drop-ball dynamic hardness test,\(^{36, 37}\) the rebound energy \(R\) can be expressed as:

\[
R = \frac{1}{2} m_p v_p^2
\]

Where \(m_p\) is the particle mass, \(v_p\) is the impact velocity, and \(e_r\) is the particle recoil co-efficiency, respectively.

In this study, \(e_r\) can be estimated as the ratio between the recoil velocity and impact velocity of the moving particle, as the following expression:\(^{38}\)

\[
e_r = \left(\frac{V_{\text{recoil}}}{V_{\text{impact}}}\right)^2
\]

Where the \(V_{\text{impact}}\) is initial impact velocity and the \(V_{\text{recoil}}\) is recoil velocity. The recoil velocity refers to the negative maximum velocity of the moving particles after impacting onto the fixed particles.

Figure 6 shows the recoil co-efficiency of TiN particles with different sizes and velocities. It can be found that TiN particles with low velocities and large sizes present higher recoil co-efficiencies than that with high velocities and small sizes. This result implies TiN particles with high recoil efficiency store up lots of rebound energies.\(^{36-38}\) When kinetic energies were high enough to result in partial fractures as shown in Figure 3, resulting in the decrease of the recoil co-efficiency.

Figure 5. Snapshots of TiN particles collision with different sizes at an impact velocity of 1500 m/s. (In fixed particle, atoms of Ti and N are colored as red and blue respectively. In moving particle, atoms of Ti and N are colored as gray and yellow respectively).
Correspondingly, particle bonding formations are regarded as bond generations between the particles. It is reported that the adhesion energy could be estimated by measuring the total energy of the simulation system. Therefore, the adhesion energy is also estimated as the following expression:*

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

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 adhesion energies and the rebound energies of TiN particle collisions with different sizes and velocities. It can be found that the rebound energies for TiN particles with different sizes were increased with the impact velocities and then were decreased at high impact velocities due to partial fractures. This phenomenon for ceramic particles was different with the metallic particles, which was increased with the impact velocities.

In contrast to the rebound energy, the adhesion energies of the nano-scale TiN particles were increased with the increase of the impact velocity. However, those particle sizes and velocities have significant effects on the relationship between the adhesion energies and the rebound energies. When the TiN particle size is 5 nm, the adhesion energy was higher than the rebound energy regardless of particles impact velocities. When the particle size is 10 nm or 15 nm, only the adhesion energy of the particles with low and ultra-high velocities is higher than the rebound energy. Those results are consistence with...
simulation results that the particles can be bonded together at low velocities due to localized atoms displacements, and partial fracturing at high velocities (as shown in Fig. 3). When the adhesion energy was less than the rebound energy at medium velocities, the moving particle was rebounded and separated from the fixed particle after impacting (as shown in Fig. 3). Those simulation results were consistent with the experimental results that nano-scale ceramic particles can be bonded together without any fragments\textsuperscript{28–31} and the sub-micro ceramic particles can be bonded together with grain refining or amorphous.\textsuperscript{16, 21–23} These results imply that nano-scale ceramic particles can be bonded together as adhesion energies being higher than rebound energies.

4. CONCLUSIONS
Collision behaviors between nano-scale TiN particles were illuminated by using Molecular Dynamics simulation through controlling the particle size and impact velocity. TiN particles after collisions show three different states that nano-scale TiN particles exhibit bonding at low velocities, bonding with partial fracturing and rebounding. A parameter selection map was summarized to provide an overview of the conditions for bonding states of nano-scale TiN particles in terms of particle sizes and velocities. Microstructures of bonded and bonded with partial fractured TiN particles obtained by simulations show that only those atoms near the impact region displaced from their equilibrium positions, while atoms far from the impact region were immobility. While the rebound TiN particles exhibit partial fractures at the impact regions. Those results imply that localized atoms displacement and partial fracture are main reasons for particle bonding formation of nano-scale ceramic particle. A relationship between the adhesion energy and the rebound energy is proposed to understand bonding formation mechanism for nano-scale TiN particle collision. Nano-scale ceramic particles can be bonded together as the adhesion energy being higher than the rebound energy.

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References and Notes

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