Molecular dynamics simulation and experimental verification for bonding formation of solid-state TiO$_2$ nano-particles induced by high velocity collision

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**ABSTRACT**

Collision processes of solid-state nano-sized ceramic particles were investigated by molecular dynamics (MD) simulation in order to clarify their bonding mechanisms. Effect of particle temperature on particle bonding formation was examined, and collision behavior of nano-sized TiO$_2$ particle was discussed in terms of particle deformations. Microstructures and bonding qualities of bonded nano-sized TiO$_2$ particles induced by high velocity collision were examined by high resolution transmission electron microscope (HR-TEM) to verify the MD results. Simulation results demonstrate that the bonding formation of nano-sized TiO$_2$ particles can be attributed to the atomic displacement and lattice distortion in localized impact region of particle boundaries. TEM microstructure results prove simulation results and indicate effective chemical bonding formations between nanoparticles at low temperature by high velocity collision. Quantitative results show that the high temperature is beneficial to the particle bonding formation. The asperity around nano-sized ceramic particles surface contributes to the displacement and lattice distortion in localized impact region under the high impact compressive pressure. The fact demonstrates a new mechanism of nano-scale ceramic particle bonding formation induced by the localized atomic displacement. The study present opens up a promising prospect of fabricating functional equipment with nano-scale ceramic particles with high velocity collision at ambient temperature.

1. Introduction

Inter-particle bonding plays a key role in determining properties of nano-porous materials. Good inter-particle bonding improves their mechanical properties [1–3] and electric properties [1,4,5]. The chemical bonding between nano-particles is mostly created by high-temperature approaches [6–8]. However, most novel functional materials are in metastable structures, which are sensitive to the conventional high-temperature sintering methods [9–11]. Therefore, a high velocity collision process can be used as a complementary approach to bond particles of those metastable materials [1,2]. Metallic particles can be bonded together by the high velocity collision when remaining at the solid phase due to their good plastic deformation abilities. For high velocity collision [2,3,12], adiabatic shears instability occurs to the particle interface, forming chemical bonding interface. However, they are lack in knowledge on the nano-particle bonding between ceramic materials with essential brittle behaviors.

Nano-ceramic materials can also present certain plastic deformation behaviors based on dislocation sliding or twinning. This phenomenon is similar to the plastic deformation of metal. Fine ceramic materials have been shown to exhibit dramatically different deformation behaviors from their bulk counterparts [13–19], although bulk ceramic is brittle and always crushed during high velocity collision [20,21]. It is well known that plastic deformation behaviors for nano-scale ceramic materials are mainly considered to be attributed to the dislocation or twinning mechanism. For example, the plastic deformations of Al$_2$O$_3$ particles [22], GaAs nano-rods [17], silica glass nano-fibers [14], calcium aluminum silicate glasses [15], and single-crystal silicon [23] under the conditions of compression, tensile and bending, are attributed to the formation of dislocations. While, the plastic deformations of Al$_2$O$_3$ micro-pillars under micro-compression [24], nano-scale body-centered cubic tungsten [25] and nano twinned Ni$_3$Al [26] are mainly attributed to twinning. Based on the dislocation or twinning mechanism, the formation of a long bonding neck needs the significant
disappearing spherical segment for the two bonded spherical particles around the bonding region. This fact leads to more longitudinal deformation of the particles. However, a “smaller is stronger” trend has been developed for single-crystal materials in micro or nano-scale [27–31]. The sample size is smaller, the stresses required to cause yield and sustain plastic flow is higher. This leads to more difficult for the nucleation and operation of dislocations or twinning. Therefore, if the disappearing spherical segment of the bonded particles is too small to cause the overall deformation of the spherical particles, it is expected that the particle bonding can be formed through some novel mechanism that shows no dependence on dislocation or twinning.

Here the inter-particle bonding formation of nano-sized TiO2 ceramic particles induced by high velocity collision was investigated. First, molecular dynamics (MD) simulation was carried out to illuminate processes of particle collisions. Microstructures of the bonded TiO2 ceramic particles were measured using transmission electron microscopy (TEM) and the bonding mechanism of the nano-scale ceramic particles during high velocity collision was discussed.

2. Experimental procedure

2.1. Molecular dynamics simulation for nano-sized TiO2 particles collision

Molecular dynamics simulation was applied to investigate the particle interface deformation during the collision process of TiO2 nanoparticles by the Buckingham-type potential [32–34]. Here, charge neutral, two spherical particles with a diameter of 3.8 nm have been cut out from a perfect anatase TiO2 crystal made of multiples of its unit cells. The applied model consisted of two TiO2 particles, i.e., a fixed particle and a moving particle (as shown in Fig. 1). Before colliding, these two spherical particles are equilibrated at different temperatures rescaling for 30 ps with a time step of 0.5 fs. Then, quality of equilibration processes of particle collisions. Microstructures of the bonded TiO2 ceramic particles were measured using transmission electron microscopy (TEM) and the bonding mechanism of the nano-scale ceramic particles during high velocity collision was discussed.

2.2. Microstructure characterization of nano-sized TiO2 particle bonding

Microstructure of the bonded TiO2 nanoparticle was investigated to confirm above simulation results. TiO2 nano-powders (P25, 25 nm, Degussa, Germany) with ambient temperature and 350 °C were deposited to from TiO2 coating onto a F-doped SnO2-glass (FTO, TEC-15, LOP) substrate using a lab-developed vacuum cold spray system [35]. For comparison, a screen-printed TiO2 coating was prepared and sintered at 500 °C for 30 mins, as reported in elsewhere [36]. Microstructures of particle/particle bonding for both the vacuum-cold-sprayed and screen-printed TiO2 coatings were characterized by transmission electron microscopy (TEM) (JEM-2100F, JEOL, Japan).

3. Results and discussion

3.1. Effect of temperature on particle temperature and particle bonding

Fig. 2 shows effect of temperature on particles temperature during collision. It can be found that the temperature of both particles immediately increased, then decreased to their original temperature. Due to the significant difference in initial temperature between the fixed and moving particles (case B of FP300K-MP773K), the temperature of the moving particle decreased and trend to the original temperature of the fixed particle in case B.

Fig. 3 shows that the neck length of the bonded particles was increased by increasing the particle temperature. This result also indicates that the atomic displacements around the compact region were increased with the increase in the particle temperature during collision. Accordingly, the particle bonding ratio can be measured as $r/R^2$, which is equivalent to the contact area ratio. By using the method described above, effect of temperature on the particle bonding ratio can be investigated as shown in Fig. 4. It can be found that the particle bonding ratio of cases of FP300K-MP300K, FP300K-MP773K and FP773K-MP773K was 0.177, 0.194 and 0.233, respectively. The present result was consistent with the result that contact area ratio for the case of in-situ particle heating during cold spraying was higher that of depositing coating at ambient temperature. On the other hand, the MD simulation result confirms that different heating approaches exist in the process of in-situ particle heating during high velocity collision. On the other hand, it clarifies that nano-scale ceramic particles can be bonded together by high velocity collision at ambient temperature.

3.2. Collision behaviors of two impacting TiO2 particle

Fig. 5 shows a trajectory and snapshots of two impacting TiO2 particle. The magnitude of the final velocity of the moving particle decreases and becomes around zero, and the distance between the two nanoparticle decreases and tends to be constant, as shown in Fig. 5(a) and (b). Fig. 5(c) shows that two TiO2 particles were bonded together even though the maximum inverse velocity. By duration of 40 ps, a separation of the two nanoparticles is also never observed over the course of simulation (as shown in Fig. 5(a)). This phenomenon indicates...
that the two particles are bonded together.

Snapshots in Fig. 5(c) show detailed bonding states. After collision starting, the atoms at the impacting region displace from their original positions, which shows localized atomic displacements. An inter-particle bonding is formed and reaches the maximum when the mass center position reaches the nearest position (1.85 ps in Fig. 5c). Later on, the particles go apart from each other due to rebound accompanied with the mass center velocity being opposite direction. Then two particles reach the farthest position where mass center velocity is zero (3.9 ps in Fig. 5c). We find clearly effective particle bonding is retained, demonstrating that the bonding is not destroyed by rebounding. After that, we further find some oscillations of the particle pair. The particle pair approaches to the equilibrium state owing to the energy dissipation. Finally, particles are accommodated with each other and the bonding neck remains a constant (similar to 40 ps in Fig. 5c). We find effectively particle bonding is retained, demonstrating that the bonding is not destroyed by rebounding.

Compared to the conventional dislocation slip or twinning mechanism, the localized atom displacement mechanism presents a brilliant advantage of no dependence on lattice orientation.

3.3. Microstructures of impacted nano-TiO$_2$ particles

To further prove this particle bonding mechanism, we examined microstructure of impacted nano-TiO$_2$ particles with surface modulations of 1–3 nm. For comparison, results of TiO$_2$ particle pairs sintered at 500 °C were also shown. In TEM images, there have different modes for the interface contact between TiO$_2$ nanoparticles, including separation, overlapping and effective bonding (as shown in Fig. 5(c)). The overlapped contact mode with Moiré patterns presents a false image of bonding and cannot be applied to judge the property of particle/particle interface contact [40]. Therefore, the reliable characterization of microstructure on the particle/particle interface can be realized by only focusing on the effective bonding mode.
Fig. 5. A trajectory and snapshots of the moving TiO₂ particle colliding with the fixed TiO₂ particle. (a–b) Trajectory of the particles collision; (c) Snapshot of the particles collision for different timesteps. (CM velocity refers to center-of-mass velocity of the moving particle; CM position refers to center-of-mass position of the moving particle. Initial temperature of both moving particle and fixed particle was 300 K and the initial particle velocity was 600 m/s).

Fig. 6. HR-TEM images of bonded nano-sized TiO₂ particle deposited by different approaches. (a) TiO₂ nanoparticle bonding modes; (b) Vacuum-cold sprayed TiO₂ coating with the particle temperature of RT; (c) Vacuum-cold sprayed TiO₂ coating with the particle temperature of 350 °C; (d) Screen-printed TiO₂ coating with the sintering temperature of 500 °C in 30 min.
Knowing this phenomenon, we can provide evident particle bonding by HR-TEM, as shown in Fig. 6(b)–(d). From the HR-TEM images, well-defined lattice fringes can be identified as the TiO₂ particles, and those nanoparticles are irregular shapes with surface roughness around 1–3 nm. It is reported that two nanoparticles were regarded as bonded together if their boundaries distance is less than a lattice parameter \[32-34\]. Therefore, two nanoparticles as shown in Fig. 6(b) are obviously bonded together after high velocity collision at ambient temperature and the boundary of the bonded particles is a step-like structure. Similarly, the HR-TEM images in Fig. 6(c) clearly show that clear bonding boundaries are formed at the interface under the collision at the particle temperature of 350 °C. This inter-particle bonding seems better than that at ambient temperature, which is similar with the microstructure of inter-particle bonding in the high-temperature processed coating following conventional sintering as shown in Fig. 6(d).

3.4. Quantitative examination the nano-sized particle bonding

To quantitatively examine the inter-particle bonding quality, a bonding ratio should be properly defined through the TEM image. In previous literature, a neck \[41\] and the distance of mass center of the bonded particles \[34\] were applied to characterize the inter-particle bonding, which is based on the assumption of the particles as regular shapes. However, TEM images show that most of TiO₂ particles have different diameters with a size distribution and particles have irregular shapes as shown in Fig. 7. To define a more precise bonding ratio of bonded particles of TEM image, we firstly draw a boundary trajectory for each particle. Then, it was supposed that the width of the boundary trajectory was equal to the lattice parameter. The length of bonding neck for two particles was considered as a bonding region diameter, and parallel lines along with the bonding diameter in the particles were considered as the particles’ diameter as shown in Fig. 7. The bonding ratio of bonded particles can be well defined as follows equation:

\[
\text{Bonding ratio} = \frac{1}{2} \left( \frac{R_a}{R_{pa}} \right)^2 + \left( \frac{R_b}{R_{pb}} \right)^2
\]

(1)

To make sure the reliability of this approach, the particle diameter was statistically examined. Results show that the particle diameter ranged from 5 to 50 nm with a mean size of 21.6 nm, which was near to the nominal diameter of 25 nm. This fact indicates that this approach is reliable for the estimation of the inter-particle bonding ratio of TEM image.

To precisely obtain the bonding ratio of TEM images, at least 50 pairs of bonded particles were examined and their bonding ratios were statistically estimated (as shown in Fig. 7). Fig. 8 shows that the bonding ratio for high temperature was higher than that for ambient temperature. This result was consistent with the performance of the dye-sensitized solar cells that electron transport resistance for the film deposited at high temperature is lower than low temperature resulting in a higher performance \[35,36\]. Those results indicate that ceramic nano-particles can be bonded together by a high velocity collision and the bonding ratio is increased with the increase of particle temperature. This result is consistent with the simulation results that particles temperature improved the particles bonding formation.

3.5. Bonding mechanisms for solid-state nano-sized TiO₂ particles

Nano-scale ceramic exhibits different deformation behavior from their bulk counterparts. In uniaxial compression tests, a size-dependent brittle-to-ductile transition for small-scale ceramic can be realized \[17,18\]. It was reported that the plastic deformation of bulk single crystals of TiO₂ (8 mm high by 3 × 3 mm cross-section) is possible at temperature above 600 °C \[42\]. The size-dependent brittle-to-ductile transition implies that plastic deformation of small TiO₂ single crystals is possible at a low temperature. Furthermore, results obtained by HR-TEM images show that nano-scale asperities present around the surfaces of TiO₂ particles (as shown in Fig. 6(b–d)). Although the incident speed is not high enough to cause bulk plastic deformation, the incident speed may be sufficient to cause deformation of those local asperities \[14,39,43-45\]. This fact indicates that the asperities around TiO₂ particles surface could be deformed under the high impact pressure as shown in Fig. 9. As consequently, nano-scale TiO₂ particles are bonded together by the high velocity collision at ambient temperature. This is different from many reported results present that submicron/micron-sized ceramic particles are always fragmented and crashed after high velocity collision \[3-5,20-22\]. Those literatures suggest that submicron/micron-sized ceramic particles are bonded together due to the fragments or amorphous induced by collision. Obviously, the nano-sized TiO₂ particle retained its integrity after high velocity collision as shown in Fig. 6. Furthermore, since the particle temperature increase...
during the collision, the deformation of the TiO$_2$ nano-particles becomes more easily at high velocity collision with a high particle temperature. The bonding formation induced by collision at high particle temperature is comparable to that for sintering at a high temperature and is higher than that by collision at ambient temperature (as shown in Fig. 6(b–d)). Those results indicate that nano-sized ceramic particles can be bonded together at a high velocity collision if having enough rough surface structures. TiO$_2$ nanoparticles could be bonded together by a high velocity collision due to the atomic displacements in the local region.

4. Conclusion

In conclusion, we have discovered a novel plastic deformation mechanism of nano-scale ceramic particle bonding formation derived by high velocity collision via MD simulation and TEM micro structural characterization. Simulation results demonstrate that the bonding formation of nano-sized TiO$_2$ particles can be attributed to the displacement and lattice distortion in localized region of particle boundaries. TEM microstructure results prove simulation results and indicate effective chemical bonding formations between nanoparticles at low temperature by high velocity collision. Quantitative results show that the high temperature is beneficial to the particle bonding formation. The asymmetry around nano-sized ceramic particles surface contributed to the displacement and lattice distortion in localized impact region under the high impact compressive pressure. Therefore, being different from conventional dislocation slip, the present study demonstrates a new mechanism of nano-scale ceramic particle bonding formation induced by the localized atom displacement. Our study opens up a promising prospect of fabricating functional equipment with nano-scale ceramic particles with high velocity collision at ambient temperature.

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References


