

An Atomistic Modeling Study of Electric Field Effect on Sintering Mechanisms of Zirconia



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Abstract This study explores the impact of electric field and temperature on flash sintering of zirconia nanoparticles using molecular dynamics simulations. The findings suggest that the electric field effect is secondary to the temperature effect. A comparison of simulations varying temperature and electric field reveals a more significant difference in diffusion coefficient with temperature variations. Furthermore, the electric field effect does not exhibit a consistent monotonic trend, as seen in the changing order of curves when temperature increases. The induced electric field contributes to crystal orientation alignment and promotes surface mechanisms throughout the sintering stages. While a higher electric field leads to greater atomic motion in the initial stage, the relationship is not strictly monotonic. However, it consistently enhances the diffusion coefficient of surface atoms, highlighting its role in surface mechanisms. Further research is warranted to fully understand the interplay between electric field, temperature, and sintering mechanisms.

Keywords Sintering mechanisms · Flash sintering · ZrO_2 · Reactive molecular dynamics

Introduction

Various methodologies exist to create materials through differing manufacturing methods. Each method has its own advantages, as well as disadvantages. One such method for creating materials is sintering. Sintering is a form of material production where a powder compact is heated to form a solid final product. Of the various manufacturing methods, sintering holds one major advantage where the material's microstructural properties may be controlled through careful consideration of various

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factors during the sintering process including particle properties, particle preparation, and sintering parameters. Because of this, sintering is a field of interest for studying since it may allow for creating a highly controlled final product [1–6].

Conventionally, sintering is a process which relies on applying heat treatment to a powder compact. By applying heat to the powder compact, once a sufficient temperature is reached within the compact, the powder will begin to melt, and the overall structure will begin to solidify. With this, given a long enough time, the original densified powder structure will become a finalized solid product. However, researchers have been studying the possibilities of field-assisted sintering, where other variables are used to enhance the sintering process in one way or another. Numerous approaches exist with the goal of promoting sintering mechanisms, for the sake of this study, field-assisted sintering will be split into two categories, pressure-assisted sintering, and electric field-assisted sintering. By applying pressure to the sample during the heating process, the particles will deform, and increase the contact area and this increase in contact area continues until local pressure is below the material yield strength [6]. With this, an external will facilitate sintering mechanisms to occur more efficiently. Electric field-assisted sintering is facilitated by applying an external electric field or current to the system which relies on rapid heating occurring due to the electricity passing through the sample [7].

With this background in field-assisted sintering, one more specific form of field-assisted sintering is called flash sintering (FS). FS is a form of field-assisted sintering where a sample has an electric field or current passed directly through the sample, and as the electric potential passes through the compact along the grain boundaries between particles, the high resistance of the material causes localized heating to occur [6, 8, 9]. A schematic showing a simplified representation of flash sintering is shown in Fig. 1.

The primary advantage of FS versus conventional sintering is typically due to a shorter sintering time and sintering temperature, which ultimately leads to lower cost for resources [10, 11]. The overall goal of FS is to achieve a comparable control of microstructural characteristics as one would have with conventional sintering methods, while using a fraction of the resources. In this study, the material of interest is zirconia, ZrO_2 , due to its favorable material properties as a ceramic with high strength and toughness at room temperature, as well as high corrosion resistance, and other forms of damage possible to the material [12]. ZrO_2 is also a material of interest due to the close structural similarity to yttria-stabilized zirconia (YSZ), which is another ceramic that has highly desirable material properties that also have a great amount of research being conducted on it as well.

Solid-state sintering is typically split into a three-step process when describing the sintering process. These steps are initial stage, intermediate stage, and final stage. The initial state is characterized by the necking area formed between two adjacent particles as the particles start creating contact between one another [13–15]. As this occurs, the pore size will decrease, and densification will increase, which is the intermediate stage [13–15]. The pore shape will change into elongated cylinders, and the grains will change into tetrakaidecahedron shapes where the pores lie along the grain edges [16], as shown in Fig. 2. In the final stage of sintering, pores are

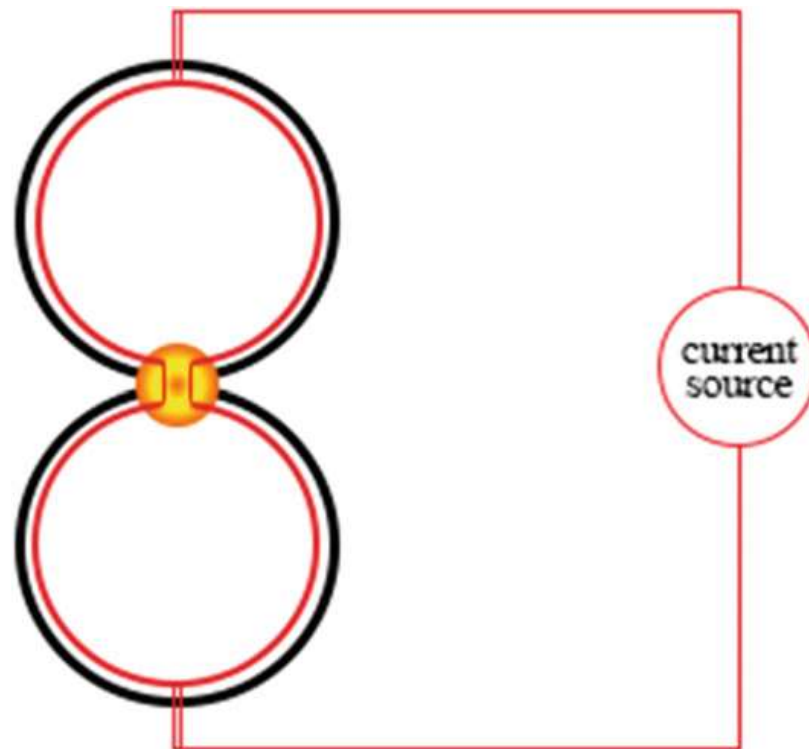


Fig. 1 A schematic of the theoretical principle of SPS heating [8, 9]

closed, and migrate towards the grain boundary junctions, and the materials are at its final state [13–15].

The simplest system possible for understanding the sintering mechanisms is a two-sphere model, where a combination of sintering mechanisms facilitates the sintering process. With solid-state sintering, these mechanisms are vapor transport, surface diffusion, lattice diffusion, grain boundary diffusion, and plastic flow, as shown in

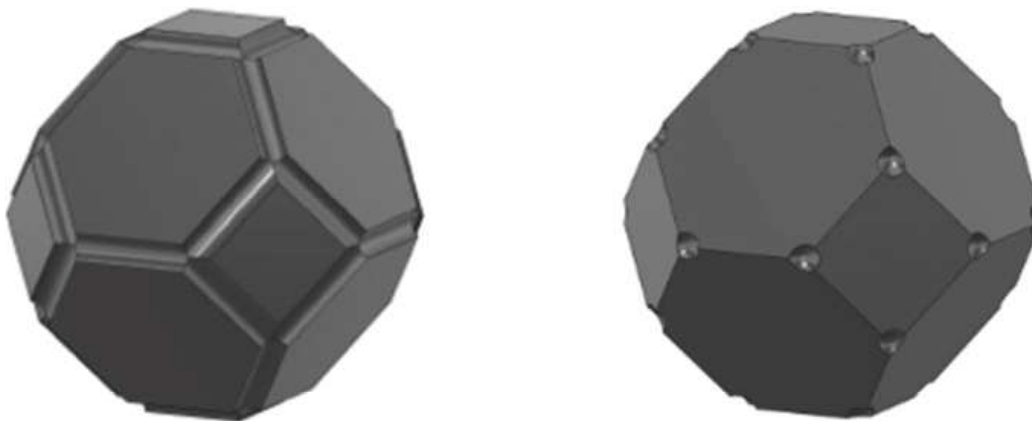


Fig. 2 Model of intermediate stage and final stage of sintering [13–16]

Fig. 2 [17]. These mechanisms are also sometimes split between the surface mechanisms consisting of vapor transport, surface diffusion, and lattice diffusion from the surface, and bulk mechanisms which consist of plastic flow, grain boundary diffusion, and lattice diffusion along grain boundaries. Surface mechanisms are non-densifying mechanisms, while bulk mechanisms will cause the two particles to coalesce.

Simulation Methods

The goal of this paper is to investigate the effect of an electric field on a two-sphere particle model for zirconia. To achieve this goal, a set of simulations will be conducted testing a range of different variables for a diverse set of simulation data to determine if a correlation exists between the effects of the induced electric field to the sintering rate of a system across one of the variables. With this, the variables of interest were the following.

Along with the varied electric field magnitude, the electric field direction was also changed between the three Cartesian directions along the x-axis, y-axis, and z-axis. The temperature values were determined based on approaching the material's melting point in the simulation. The two-particle sizes were chosen based on the computational capability of the available machines for use with conducting the simulations relative to the timeline for the research. Finally, the electric field strength was determined using a range of values that has seen favorable results in both simulations and experiments for similar systems [18, 19].

The simulation model was made by creating a similar two-particle system to Fig. 3, where each spherical particle was initially created in LAMMPS [20] with a vacancy percentage of approximately 4%. Each structure was moved from LAMMPS into Amsterdam Modeling Suite (AMS) [21], where the full MD simulation [6, 22–24] was conducted using a ReaxFF engine [21]. The particle was preheated from zero kelvin to the final desired temperature linearly over 40,000 steps with a timestep of 2.5 fs. The particle was given up to 10,000 steps of soaking at this final temperature. As a result, Fig. 4 shows the obtained models of 3 nm and 5 nm ZrO_2 particles.

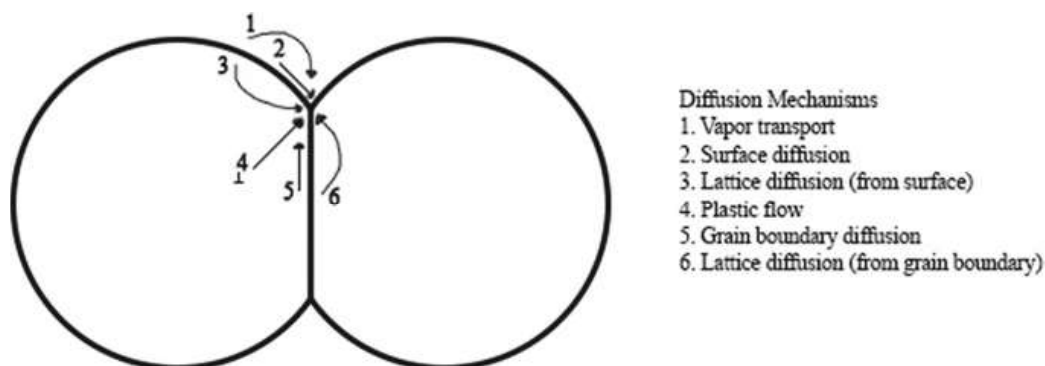


Fig. 3 Visualization of how the various diffusion methods contribute to sintering [17]

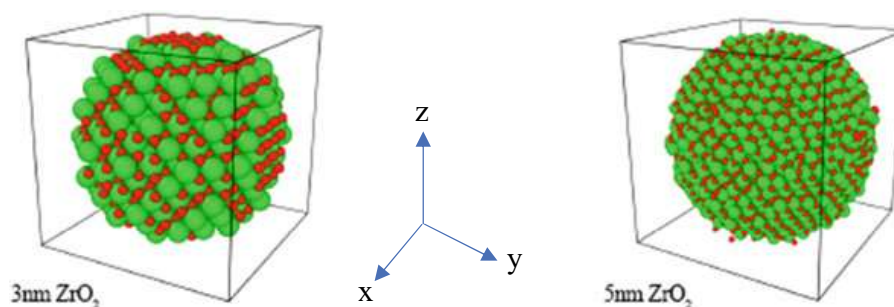


Fig. 4 3 nm and 5 nm zirconia single-particle initial models

Table 1 Overview of zirconia simulation variables

Temperature	1300 K	1500 K	1700 K
Particle size	3 nm	5 nm	
Electric field	0 V/cm	500 V/cm	1000 V/cm

The two-particle system was created by duplicating the preheated single particle and mirroring it to create the desired system. The two-particle sintering simulation took place at the desired temperatures shown in Table 1 and simulated with 300,000 steps, and a timestep of 2.5 fs. This initial two-particle system is shown in Fig. 5.

The desired field-assisted sintering system was created by introducing an electric field into the two-particle system. This electric field was introduced with the goal of modeling a similar phenomenon for contactless FS seen in other studies [25]. However, this contactless FS is largely different from our simulated system. In our mode, we do not have arc facilitating the sintering, only electric field effect is introduced to our model system.

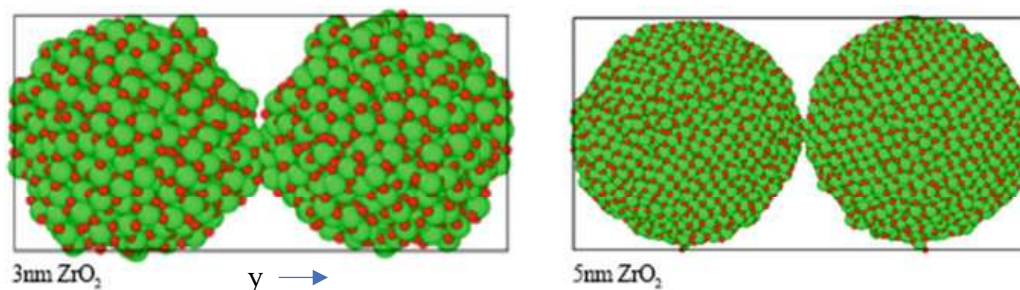


Fig. 5 3 nm and 5 nm zirconia two-particle models

Results and Discussion

Sintering was quantified as a function of the change in neck area between the two particles where, as a sintering simulation continues, the necking area between two particles will ideally increase until it reaches a point where the neck area is the same as the particle diameter. It was observed that an introduced electric field does influence the simulation. However, when tested between different electric field magnitudes and directions, it was found that most importantly, as the temperature increases, the relative contributions of the electric field to the sintering rate decrease.

Regarding atomic motion, it was found that the effects on sintering for the introduced electric field are most prominent during the early stages of sintering. During the initial phase of sintering, the displacement vector figures show that it is most common for the greatest increase in atomic motion to occur under the influence of an electric field induced in the Cartesian direction adjacent to the two particles. Further analysis does show; however, this may be due to the initial particle orientation. This increase in motion during the initial phase of sintering is shown in Fig. 6. With this, it's possible that the induced electric field promotes the alignment of the particles.

It was also found that the simulation results align with academic findings which suggest an Arrhenius relationship between the diffusion coefficient and the temperature. While under the influence of an electric field, plotting the Arrhenius relationship shows that the overall system diffusion coefficient does not greatly change with an applied electric field. Also, the applied electric field seems to have a weaker effect on the overall system as the temperature increases. Lastly, the relationship between the electric field and the system's diffusion coefficient is unclear as, in some cases, it increases the diffusion coefficient. In contrast, in other cases, the diffusion coefficient decreases under an electric field's influence.

With the seemingly larger effect of the electric field's contribution on earlier stages of sintering, as well as analysis of surface atoms, it can be concluded that during the

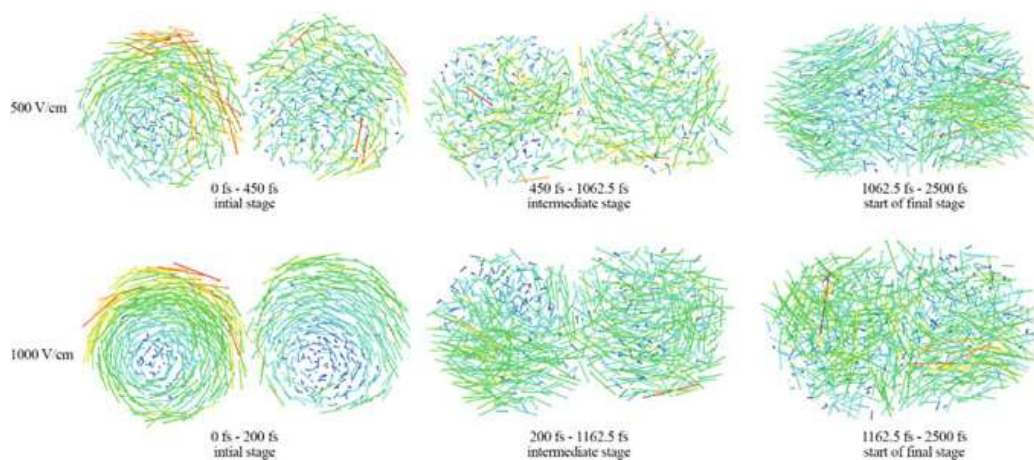


Fig. 6 Flash sintering displacement vectors for 3 nm ZrO_2 at 1500 K with an electric field applied in the y-direction

initial stages of sintering, the influence of the electric field is more significant in the surface atoms. With all of this, it's possible to conclude that the induced electric field contributes to increasing the diffusion rate of a system by promoting surface sintering mechanisms.

Conclusion

Overall, it was found that, while under the influence of an electric field, the sintering rate does change, it is a minor effect when compared to the far larger effect the temperature has on the overall sintering rate. This effect may not be monotonic, as sometimes it causes an increase or a decrease in sintering rate. The overall contribution of the electric field to the sintering rate remains ambiguous as sometimes it yields an increase, while other times it yields a decrease. It's been seen that the electric field's effect on the sintering rate is most prominent during the early stages of sintering, between surface atoms. With this, the effect of the electric field facilitates surface sintering mechanisms. While these conclusions hold true for zirconia, more research should be conducted into different materials, a larger sample size, larger range of temperatures and electric fields, a different number of particles, different particle positions, different particle sizes, deeper analysis into the possible changes of crystal structure, and many more possible variables. Overall, the conclusions found can be further expanded with more research into this field of flash sintering with the introduction of more closely monitored variables and careful analysis.

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Data Availability The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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