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ORIGINAL PAPER

Energetic performance of reactive metal nanoparticles: Computational materials research integrated with science pedagogy

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Abstract
We aim to develop and implement a program using reactive modeling dynamic (RMD), one type of computational modeling and simulation techniques, to help college students learn chemical reactions in materials science. Prior to the first implementation of the program, four college students from different engineering majors were selected and trained with RMD, research, and leadership skills utilizing our pedagogical approach. The current study presents the findings of their culminating projects as outputs, where students generated inquiry from their own experiences leading to authentic questions and opportunities to explore and discover material processes. The energetic performance of various metal nanoparticles using RMD is presented and discussed.

Introduction

In recent years, metal nanoparticles have attracted a great amount of attention in the community of energetic materials owing to their high energy density, high reaction rate, and earth abundance [1]. Recent studies confirmed that a wide range of metal nanoparticles such as Pt, Co, and Al elements can be used as promising fuel resources for solid rocket motors [2, 3]. As such, revealing the energetic performance of the metal nanoparticles is critically important to leverage solid-fuel-based aerospace applications. To prepare future scientists and increase the pursuit of materials science among college students, various efforts have been made in higher education such as introducing materials science topics in engineering courses. However, students often find these topics challenging. Understanding chemical reactions is a crucial aspect of materials research, yet many students struggle due to the abstract nature of chemistry. A reasonable approach to address this concern is to utilize computational modeling and simulations (CMS) techniques to help students visualize unobservable phenomena for advanced materials research [4, 5]. In this context, the overall goal of our project is to develop and field-test a co-curricular program that equips engineering students with CMS skills to enhance their basic knowledge of chemistry and its application in reactive materials engineering. As part of the project and before the first program implementation, we trained four college students who had prior experiences in computer simulation or related skills, demonstrated potential in research, and wished to continue scholarly work and pursue a higher degree in science, technology, engineering, and mathematics (STEM). The current study presents research findings related to reactive materials engineering led by the students we trained.

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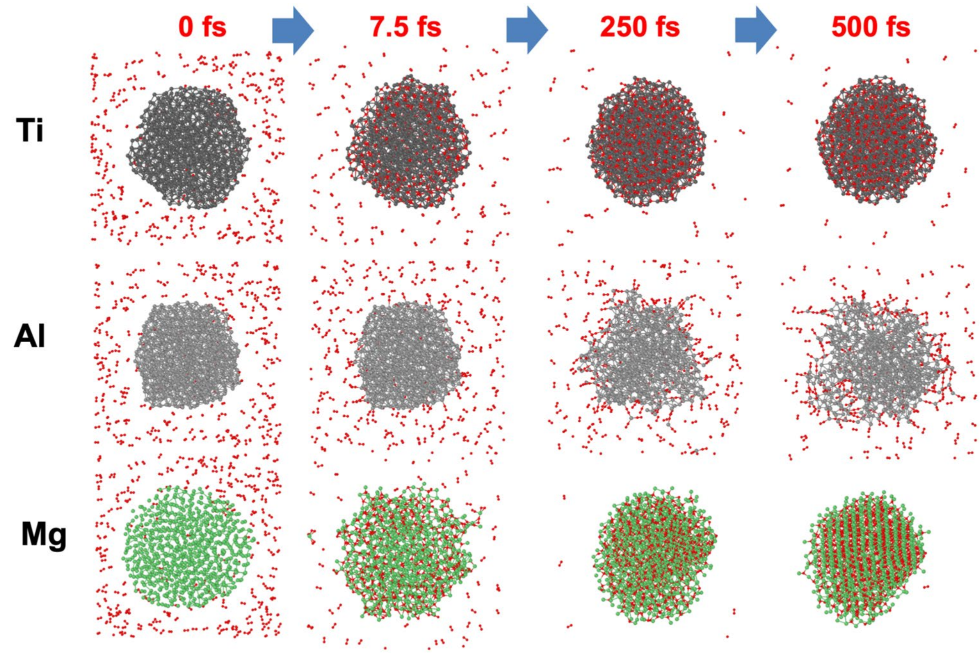

Fig. 1 Structural evaluation of single metal nanoparticles (Ti, Al, and Mg) during the oxidation process. Note that the Ti nanoparticle showed a faster reaction, when compared to Mg and Al nanoparticles. Atomic legends (Ti: dark gray, Al: light gray, Mg: green, and O: red)

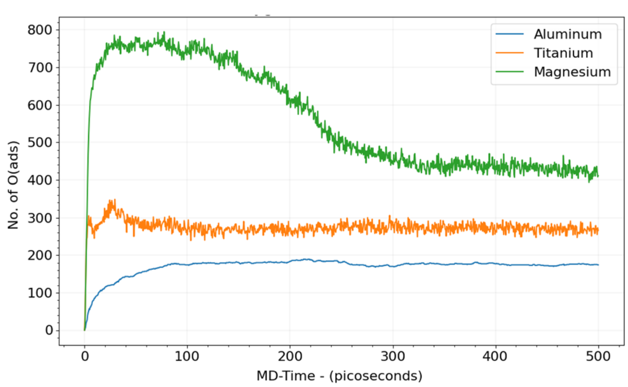

Fig. 2 The number of adsorbed O atoms during the metal oxidation

Research methods

Instructional details

We utilized reactive molecular dynamic simulations (RMD), one of the CMS techniques, to investigate physical and chemical properties of nanoscale structures. RMD provides dynamic representations and manipulation of abstract and unobservable phenomena (e.g., chemical reactions at a molecular level), allowing them to build molecular structures, run atomistic simulations, and visualize and analyze simulation results. Four college students (gender: female = 2; ethnicity: Hispanic = 2 and South Asian = 2) were trained in RMD using an inquiry-based instructional framework and other evidence-based science strategies to analyze the energetic performance of metal nanoparticles. Three project faculty in engineering and STEM education conducted weekly meetings via Zoom and in person to provide ongoing support on learning strategies, time management, a sense of belonging, and a growth mindset to help the students become strategic learners in their own majors. The students were actively involved in project activities including the preparation of instructional materials and reviewing and simulating the program. Furthermore, the students developed their own research topics in STEM, related to their majors (e.g., RMD simulations of the oxidation of metal nanoparticles) and explored areas they wish to study in-depth, preparing themselves for professional careers in STEM fields.

Computational details

In this work, multiple ReaxFF [6] force field parameters (Al–O, [7] Ti–O, [8] Mg–O [9]) for three metal nanoparticles (Al, Ti, and Mg) were used respectively, coupled with RMD simulations. The RMD simulations were conducted by a commercial software, Software for Chemistry & Materials (SCM) Amsterdam Modeling Suit. Each nanoparticle was prepared using the following procedure: 1. expanding the unit cell structure of each crystal phase (i.e., ~ 1000 atoms); 2. cutting the supercell structure to a spherical shape via ATOMSK software [10]; 3. running thermal relaxation of the spherical particle at 500 K up to 12.5 ps where the nanoparticles transformed from the fully crystal to the amorphous structure. As a result, we

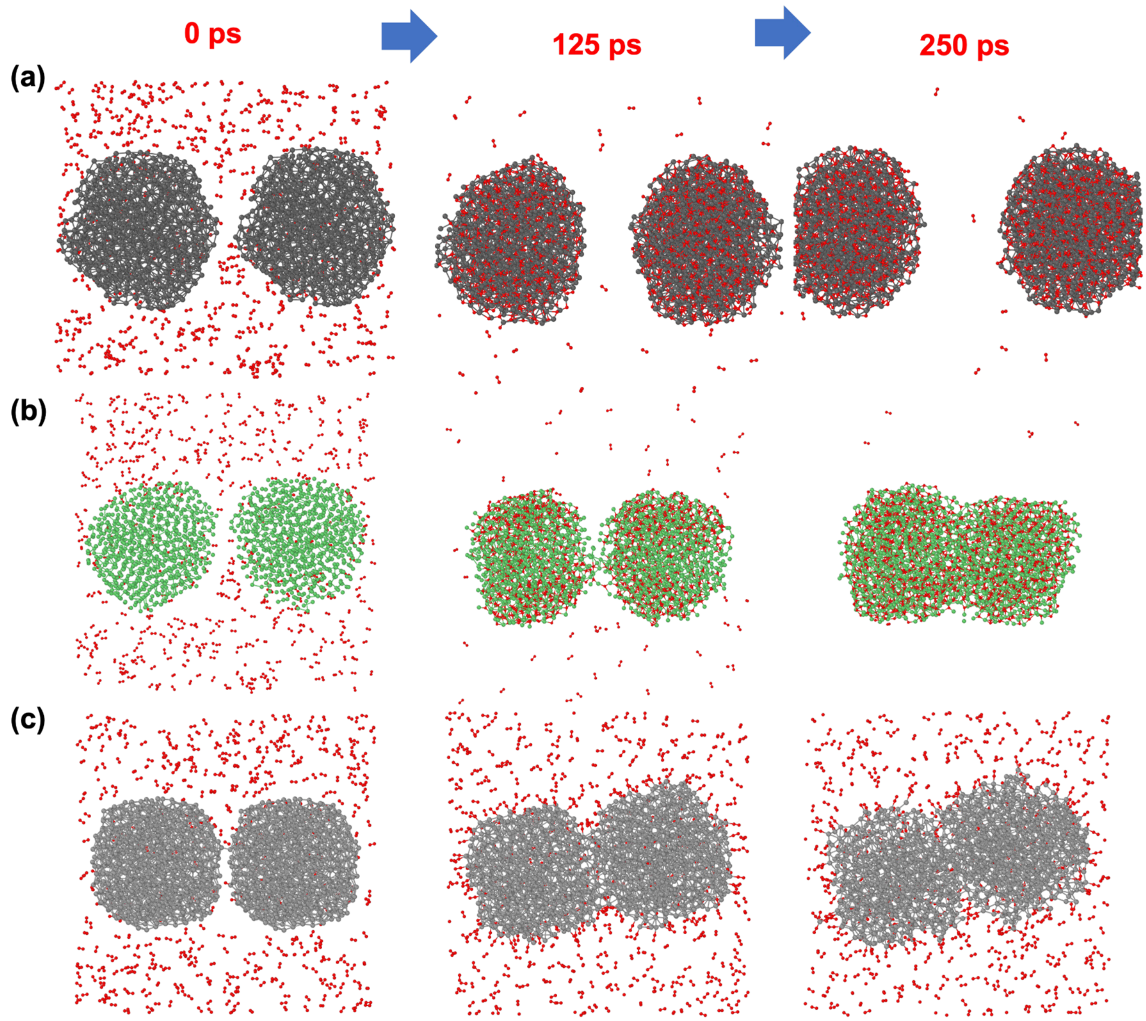

Fig. 3 The oxidation of dual metal nanoparticles: **a** Ti nanoparticles, **b** Mg nanoparticles, and **c** Al nanoparticles. Note that all nanoparticles underwent the sintering during the oxidation process while the sintering of the Al nanoparticles occurred at the earlier stage (i.e., t < 125 ps) when compared to other particles which resulted in decreasing the surface-to-volume ratio of metal nanoparticles, and thus lowering the oxidation rate

were able to generate the initial nanoparticle for the oxidation process. Two separate simulations were conducted: 1. single metal nanoparticle with oxygen molecules; and 2. dual metal nanoparticles with an increased amount of oxygen molecules. The system density of both cases was 0.5 g/cm^3. The system density refers to the density of the entire simulation cell. We used a bit higher system density, when compared to experimental conditions to observe the reaction processes quickly. Then the entire system was gradually heated from 300 to 1000 K using a Nose–Hoover thermostat. The system was heated with the first simulation for 2,000,000 steps and later simulation for 500,000 steps. A time step of 0.25 fs with a temperature damping constant of 100 fs was employed. The size of the simulation cell was 80 Å × 80 Å × 70 Å.

Results and discussion

In order to understand the molecular interactions of three different metal nanoparticles, we performed ReaxFF-RMD simulations by thermally accelerating the oxidation process which emulates the combustion reaction in a fuel-rich oxygen environment. One of the main purposes was to compare the oxidation rate between the different metals. Figure 1 shows that the oxidation rate was the fastest among Ti and Mg metal nanoparticles followed by a lower rate in the Al nanoparticle. This can be understood by the fact that the oxidation rate of metal nanoparticles depends on the reaction kinetic of each metal and O element. Namely, Ti–O interaction is a thermodynamically favorable reaction than Mg–O or Al–O interaction. We also found that the relatively thick oxide layer on the Al surface resulted in creation of

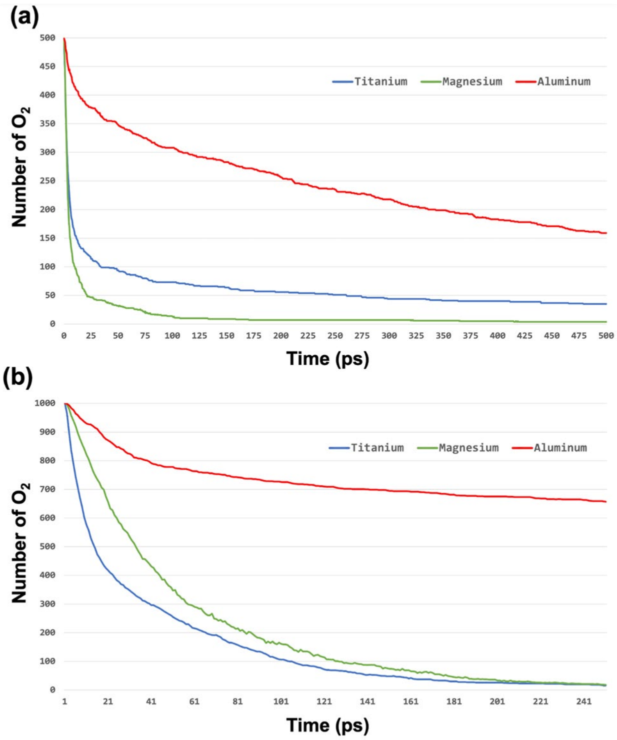

Fig. 4 The oxidation rate of three nanoparticles; **a** single nanoparticle with oxygen; **b** dual nanoparticle with oxygen

long chains of oxygen on the surface of Al nanoparticle. (See the Al oxidation at 250 ps in Fig. 1). This limits the number of O_2 molecules that can further be penetrated into the subsurface of Al nanoparticle. Figure 2 further confirms this discussion. Namely, the increased number of adsorbed O atoms was found in Ti/Mg nanoparticles, when compared to Al nanoparticle, leading to the formation of the oxide layer on the sub-surface of metal nanoparticles. Note that the number of adsorbed O atoms increased very quickly and then decreased after 50 ps. This may be attributed the fact that the suboxide layer turned into the oxide layer.

To see if the nanoparticles' aggregation affects the oxidation process, we also performed RMD simulations of the oxidation of dual nanoparticles as shown in Fig. 3. The initial separation between two nanoparticles was set by 2.5 Å. This was based on our thorough trial-and-error simulations while varying the initial separation ranging from 1.0 to 5.0 Å. We found that the initial separation of 2.5 Å was a reasonable choice because the bond analysis from our ReaxFF simulations confirmed that two nanoparticles were not chemically bonded. Please note that Ti dual nanoparticles underwent the fastest oxidation when compared to Mg or Al dual nanoparticles, consistent with the oxidation of the single nanoparticle. Interestingly, the difference between Ti/Mg and Al oxidation rates increased further when the system contained multiple particles (See Fig. 4a and b). This may be attributed to the fact that bare Al nanoparticles are easily sintered while less sintering effects were observed in Ti/Mg nanoparticles (See Fig. 3). That is, the sintering of metal nanoparticles decreased the surface-to-volume ratio, making the oxidation reactions slower. As such, it can be suggested that Ti nanoparticles can act as a more energetically efficient fuel agent. It should be mentioned that the primary aim of this research work is to let college students perform computational modeling and simulations and analyze their simulation results to help students strengthen their view toward material science and engineering. As such, the validation of the simulation results with experimental results was limited by students' ability to possess RMD skills at the entry level. However, the results drawn from ReaxFF based RMD simulations were previously well validated with experimental results [6].

Conclusion

In summary, four holistically trained college students conducted the RMD to demonstrate the oxidation of the metal nanoparticles, examined RMD snapshots, and analyzed the energetic performance of each particle. Findings of the RMD simulations revealed that the oxidation rate of metal nanoparticles relies on the chemical reactivity of metal–oxygen elements which will potentially lead to different energy releases during the oxidation processes. This study will be expanded to investigate the different oxidation kinetics and mechanisms of each nanoparticle as well as the energetic information. We believe our efforts in preparing student scholars with up-to-date technology and pedagogy will make a significant contribution to diversifying the community of computational materials research.

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Author contributions J. H., S. H., J. S. designed research and supervised the project. P. L. conducted simulations, analyzed the results, wrote a manuscript. A. V. conducted literature review. K. F. conducted chemical modeling. M. T. managed a training schedule. All authors contributed the development and refinement of program modules.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare that there is no conflict of interest to declare.

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