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Study of nickel-coated aluminum nanoparticles using molecular dynamic simulations and thermodynamic modeling

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Abstract Aluminum nanoparticles have widely been used as fuel additives to solid propellants for rocket propulsion, but the formation of the oxide layer has been a setback for their application. A viable solution to this problem is to passivate aluminum (Al) with a layer of nickel (Ni), which offers multiple advantages. The current study focuses on energetic intermetallic interaction within Ni-coated Al nanoparticles and also the interaction/coalescence between two Ni-coated Al nanoparticles of varying sizes. Molecular dynamics (MD) method is employed to study the size-dependent variation of these interactions.

A thermodynamic formulation is devised to calculate the adiabatic reaction temperature of single as well as coated nanoparticles. The results obtained using this formulation are compared with the results obtained from MD simulations. The estimation of dead layer thickness formed at the interface of Ni and Al is critical to correctly capture the energetic behavior. In this work, the dead layer thickness is estimated and used to predict the adiabatic reaction temperature of the coalescence of two equal-/unequal-sized Ni-coated Al nanoparticles. It has been found that particle size can affect the adiabatic reaction temperature because of the varying surface energy. It has also been found that the dead layer thickness plays a vital role in accurately determining the adiabatic reaction temperature of the system. It has been observed that the reaction time decreases proportionately with increase in specific reaction surface area (between Al and Ni) for single as well as coated particles.

Introduction

Aluminum, in the form of microscopic spherical particles, has been widely used as a fuel additive to solid-propellant rockets because of its low cost, high energy density, and high combustion temperature (DeLuca 2018). However, nascent aluminum, being a reactive metal, reacts in an oxidizing environment to form aluminum oxide (Al_2O_3)/alumina layer of thickness 2–5 nm over its surface (Trunov et al. 2006). The formation of alumina layer results in high ignition temperatures (Friedman and Maček 1962) of micron-sized aluminum particles owing to its high melting temperatures ($\sim$ 2350 K). Moreover, the alumina layer also causes agglomeration of aluminum within solid

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rocket motors during combustion (Andrzejak et al. 2007). This leads to incomplete combustion and slag formation creating hindrance in steady and complete combustion, which in turn reduces efficiency of fuel combustion.

Nanoparticles garnered interest of the scientific community due to their unique thermo-chemical properties. They exhibit low melting temperature, high chemical reactivity, and shorter characteristic times, owing to a large surface to volume ratio, in comparison with bulk counterparts. These characteristics make nanoparticles a promising choice in the areas where a sudden surge of energy is desired. Inclusion of aluminum (Al) nanoparticles to the solid propellant instead of micron-sized Al particles has shown to improve combustion performance significantly. Nonetheless, the formation of alumina layer remains an issue (Sundaram et al. 2015).

The alumina layer does not constructively aid the properties of Al nanoparticles for the aforesaid reasons and is often considered as *dead weight*, whose reduction or elimination would be helpful in exploiting the favorable characteristics of Al (Foley et al. 2005). Removing the alumina layer would not be a viable solution for several reasons. Passivating aluminum surface with a thin layer of material whose melting temperature is less than that of alumina is considered to be an effective method to reduce the ignition temperature of particles significantly. Contrary to alumina, the passivated metal coatings could promote the reactivity of Al at elevated temperatures and undergo inter-metallic reactions with the underlying Al, releasing heat in the process that can then aid in combustion (Foley et al. 2005; Yavor and Gany 2008). Studies have shown that Ni is a potential candidate for coating Al surface in precluding the formation of alumina layer (Foley et al. 2005), thereby reducing the ignition temperature (Shafirovich and Varma 2004) because of its lower melting point temperature than alumina. Moreover, it also reacts exothermally when alloyed with Al, and the heat of exothermic reaction results in the enhancement of the ignition of Ni-coated Al nanoparticles (Shafirovich and Varma 2004; Andrzejak et al. 2007).

There have been many works addressing the melting and sintering of Al nanoparticles, but the area of Ni-coated Al nanoparticles is largely underexplored. Hanyaloglu et al. performed a study on Ni-coated Al powder and found that when the powder was slowly heated, it melted at 913 K and provided a means for rapid diffusion of Al and Ni particles. A great amount of heat was eventually released during the formation of intermetallic compound through exothermic reactions (Hanyaloglu et al. 2001). Lewis et al. (1997) found that the coalescence of Ni-coated Al takes place in two stages. In the first stage, the contact area is maximized and in the second stage, "sphericization" takes place, which is driven by surface diffusion. It was observed that the first stage proceeded very rapidly in comparison with the second stage. Sundaram et al. (2013) studied the thermochemical behavior of Ni-coated Al particles in size range of 4–18 nm using MD simulations. It was found that the melting point of coated particles was higher than the nascent Al due to cage-like mechanical constraint placed by the Ni shell. The melting point and adiabatic temperature were observed to rise with an increasing Al core size. Henz et al. (2009) analyzed the energetic reactions of Ni and Al system by considering two cases: the coalescence of Ni-Al, and Ni-coated Al nanoparticle. It was observed that reaction times tend to decrease and adiabatic reaction temperatures increase with a decrease in nanoparticle size.

The objective of the present work is to develop a thermodynamic model to accurately predict the adiabatic reaction temperature of Ni-coated Al nanoparticles. The accurate prediction of the adiabatic reaction temperature demands the *dead layer thickness*, i.e., thickness of reacted Ni-Al at the interface of Ni-coated Al nanoparticle, to be determined in advance. The first part of the present study focuses on developing the model and verifying it with the data obtained by simulating the energetic reaction between two separate Ni and Al nanoparticles. The genesis of the present formulation can be credited to the research carried out by Henz et al. (2009). A similar model is devised to predict the *dead layer* thickness of Ni-coated Al nanoparticle. The model is then used to predict the adiabatic reaction temperature and reaction time in the coalescence of two Ni-coated Al nanoparticles in the range of 4 to 6 nm. Reaction time is computed based on the time taken for a certain temperature rise during the energetic reaction. A model is developed relating the reaction time and the specific reaction surface area, and is tested for single and separate Ni-coated Al nanoparticles.

Simulation approach

In the present work, the classical molecular dynamics (MD) (Alder and Wainwright 1959) method is employed to study the coalescence of Ni and Al nanoparticles. In MD simulation, we treat materials under consideration as an aggregation of discrete particles like atoms or molecules which interact by exerting forces on each other via an interatomic potential and follow the classical Newtonian equation of motion. The main idea of MD simulation is to describe the time evolution of a system of interacting particles by integrating their equations of motion. It gives information about the positions and velocities of every particle in the system. A more comprehensive description of the method is found elsewhere in Allen and Tildesley (1989). In the present work, an open-source MD code LAMMPS (Plimpton 1995) (Large-scale Atomic/Molecular Massively Parallel Simulator) is used to perform MD simulations on several (60-i-120) Intel Xeon E5-2670 processors.

In the current work, Embedded Atom Method (EAM) potential has been applied to simulate the various interactions of Ni and Al atoms. EAM potential, developed by Daw and Baskes (1983), is a semi-empirical, many-body potential especially suitable for modeling realistic metallic systems. Further details of the EAM potential can be found elsewhere (Daw and Baskes (1983)). The MD simulation results are compared with the formulation developed with the help of a thermodynamic analysis of the system. The primary nanoparticles considered for the first part of this work i.e., the sintering of separate Ni and Al nanoparticles containing 382, 1291, and 3061 atoms. This corresponds approximately to Ni nanoparticle of diameters 2 nm, 3 nm, and 4 nm, respectively. These diameters were chosen based on the computational time required for their simulation. In this case, the nanoparticles are modeled by defining a spherical region in the simulation domain and then materials are placed within the region of different radii considered in this work. Al nanoparticles are modeled by placing the fcc structure of lattice constant 4.05 Å and Ni nanoparticles by placing the fcc structure of lattice constant 3.52 Å in their respective spherical regions of the corresponding radius.

While performing molecular simulations for Ni-coated Al particles, the smallest core diameter used was 4 nm. The simulations were performed on nanoparticles containing 2018, 2874, 3942, 5247, and 6812 atoms each of Ni and Al with Ni acquiring the shell part and Al forming the core. Core-shell nanoparticles are modeled by initially preparing a spherical Ni nanoparticle and then making a concentric spherical cut inside the particle of the desired radius. The shallow region is filled with Al particle of the corresponding radius (Sundaram et al. 2013; Henz et al. 2009). The way in which both separate and core-shell nanoparticles are modeled is similar to making a spherical cut in the bulk material. This results in excess energy of the surface atoms compared with the interior atoms. To obtain a stable equilibrium configuration of the nanoparticles, we have employed conjugate gradient minimization technique followed by the equilibration process of the particles so that the total energy does not change with time (Leach and Leach 2001). During equilibration, the total energy undergoes a transient phase initially and then remains constant with time. Noteworthy is the fact that constructing an accurate initial structural configuration, especially for the core-shell nanoparticles, is a critical as well as a challenging task. As mentioned before, for single nanoparticles, we have made the initial configuration by making spherical cuts in the bulk lattice followed by the equilibration process to achieve the minimum energy configuration of nanoparticle. It may be noted that with this approach, extra potential energy may still be present as the system may not be able to attain a global minimum energy state. An alternate approach is to use truncated octahedron to resemble a quasi-spherical cluster, so that the appropriate surface facets generate minimum surface energy and stable equilibrium structure (Baletto et al. 2002). Additionally, for core-shell nanoparticles, we have constructed a sharp interface between the core and the shell, though intermixing between Ni and Al atoms is expected for such systems. Furthermore, an initial lattice mismatch between the core and the shell can lead to surface reconstruction. Hence, there is a scope to further improve the model by incorporating a more intricate method to construct the initial configurations.

Coalescence of separate nickel and aluminum nanoparticles

Thermodynamic analysis

A thermodynamic model is devised to estimate adiabatic reaction temperature of the coalescence of Ni and Al nanoparticle system (see Fig. 1). The system under consideration is an equimolar Ni and Al particle and the reaction is assumed to be adiabatic. The results obtained through the model are used to compare the MD simulation results.

The reaction that is followed for this process is as follows:

$$nNi + nAl \rightarrow nNiAl \tag{1}$$

Here, n is number of moles, Ni and Al represent nickel and aluminum nanoparticles, and NiAl is nickel aluminide which is the product of the reaction.

For an adiabatic process, the enthalpy of reactants must be equal to the enthalpy of products.

$$H_{reactants} = H_{products} \tag{2}$$

The coalescence process is initiated at 400 K. The enthalpy of reactants is calculated as:

$$H_{reactants} = H_{Al,400K} + H_{Ni,400K} + H_{Al,surf} + H_{Ni,surf} \tag{3}$$

The equation can be rephrased as follows:

$$H_{reactants} = n\left(\bar{h}_{Al,400K} + \bar{h}_{Ni,400K}\right) + H_{Al,surf} + H_{Ni,surf} \tag{4}$$

where molar enthalpy $\bar{h}(T)$ is given as:

$$\bar{h}(T) = \bar{h}^{\circ}_{form,298K} + \int_{298}^{T} \bar{c}_p(T)\, dT \tag{5}$$

The enthalpies of formation of Al and Ni at 298 K are $\bar{h}^{\circ}_{Al,form,298K} = 0\, kJ/mol$ and $\bar{h}^{\circ}_{Ni,form,298K} = 0\, kJ/mol$. $\bar{h}_{Al,400K}$ and $\bar{h}_{Ni,400K}$ are molar enthalpies respectively of Al and Ni at 400 K (which are at solid state), and are obtained by considering the variation of specific heat capacity c_p (Kubaschewski et al. 1993) with temperature.

The bulk specific heats (in kJ/mol K) of Ni and Al respectively are given as:

$$c_{p,Ni}(T) = 0.01117 + 0.00003778\, T + 318\, T^{-2} \tag{6}$$

$$c_{p,Al}(T) = 0.03138 - 0.00001640\, T - 360\, T^{-2} + 0.00000002075\, T^2 \tag{7}$$

Now, based on Eqs. 5 to 7, the values of $\bar{h}_{Al,400K}$ and $\bar{h}_{Ni,400K}$ are 2.569 kJ/mol and 2.756 kJ/mol, respectively. The unit of temperature in Eqs. 6 and 7 is Kelvin.

Fig. 1 A schematic showing the coalescence of Ni and Al nanoparticles
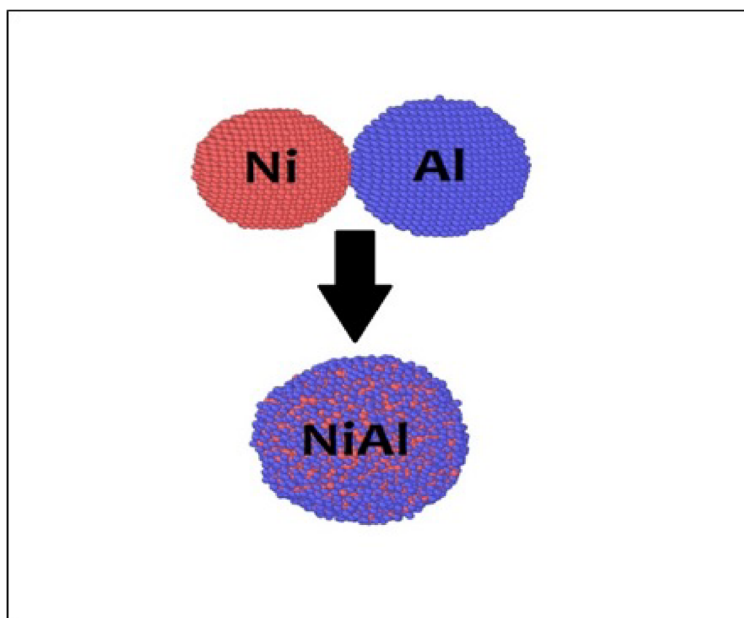
In Eq. 4, $H_{Al,surf}$ and $H_{Ni,surf}$ represent enthalpies due to uncoordinated atoms on the surface of Ni and Al (i.e., surface energy).

Similarly, the enthalpy of products is calculated (assuming NiAl is in molten state) as:

$$H_{products} = H_{NiAl,T_{ad}} + H_{NiAl,surf} + H_{NiAl,melt} \quad (8)$$

$$\overline{h}_{NiAl}(T_{ad}) = \overline{h}^{\circ}_{NiAl,form,298K} + \int_{298}^{T_{ad}} \overline{c}_{p,NiAl}(T)\, dT \quad (9)$$

$$H_{products} = n\left(\overline{h}^{\circ}_{NiAl,form,298K} + \int_{298}^{T_{ad}} \overline{c}_{p,NiAl}(T)\, dT + \overline{h}_{NiAl,melt}\right) + H_{NiAl,surf} \quad (10)$$

$$c_{p,NiAl}(T_{ad}) = 0.04184 + 0.00001381\, T_{ad} \quad (11)$$

where $\overline{h}^{\circ}_{NiAl,form,298K} = -118.4\ kJ/mol$ and $\overline{h}_{NiAl,melt} = 62.8\ kJ/mol$. T_{ad} is the adiabatic temperature, which needs to be determined. The values of enthalpy of heat of formation and enthalpy of melting of NiAl are taken from "Materials Thermochemistry" (Kubaschewski et al. 1993).

In Eqs. 4 and 10, the enthalpy of particles due to their surfaces is computed for Ni, Al, and NiAl as follows:

$$H_{Ni,surf} = \sigma_{Ni} \cdot a_{Ni} \quad (12)$$

$$H_{Al,surf} = \sigma_{Al} \cdot a_{Al} \quad (13)$$

$$H_{NiAl,surf} = \sigma_{NiAl} \cdot a_{NiAl} \quad (14)$$

The values of surface energy per unit area, σ_{Ni}, σ_{Al} and σ_{NiAl}, are 2273 mJ/m^2 (Nizhenko 2004), 942.2 mJ/m^2 (Leitner et al. 2017), and 1400 mJ/m^2 (Lozovoi et al. 2000; Miracle 1993), respectively. The surface areas of Ni and Al are computed by their respective densities and of NiAl by conserving the masses and volumes of Ni and Al, respectively.

The change in surface energy is an important parameter that affects the coalescence process and is formulated as:

$$\Delta H_{surf} = H_{NiAl,surf} - (H_{Ni,surf} + H_{Al,surf}) \quad (15)$$

The change in surface energy is a major factor in determining the adiabatic reaction temperature of the system. It is interesting to note that as the particle size increases, the reduction in surface energy per unit mole of NiAl decreases, as shown in Fig. 2. This is because, as the size increases, the fraction of atoms/molecules on the surface decreases. This results in a subdued effect of surface energy on the properties for larger particle sizes.

Adiabatic reaction temperature of the system is obtained by substituting all the values of available parameters in Eqs. 2, 4, and 8, and also by considering the variation of specific heat of NiAl with temperature (Kubaschewski et al. 1993), as shown in Eq. 11.

Table 1 shows the adiabatic reaction temperature obtained through a thermodynamic model for equimolar system of Ni and Al. It can be noted that the adiabatic reaction temperature increases with decrease in particle size. This can be attributed to larger reduction in surface energy per unit mole of NiAl for smaller particles during the coalescence process (see Fig. 2).
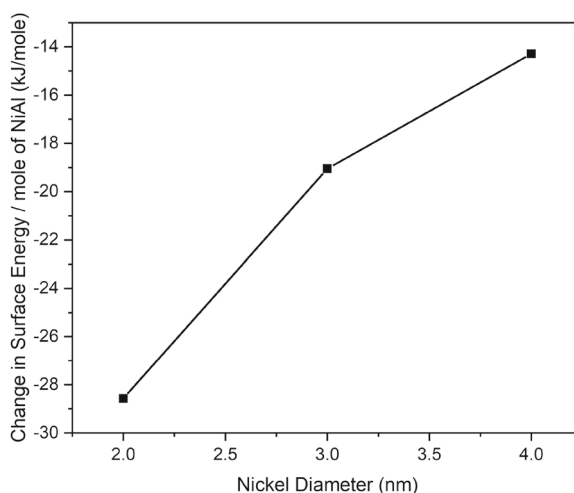

Fig. 2 Variation of change in surface energy with Ni nanoparticle diameter

MD simulation results

The MD simulations are used to model adiabatic coalescence of Ni and Al nanoparticles, with a constant number of atoms and constant total system energy. Figure 3 shows the time evolution of coalescence of Ni and Al nanoparticle system through MD simulations.

Figure 4 shows the adiabatic reaction temperature obtained through MD simulations and the temperature predicted through thermodynamic analysis of the particles, as discussed in the previous section.

The purpose of these simulations is to analyze the effect of nanoparticle size on the adiabatic reaction temperature and thus on the coalescence process of Ni and Al nanoparticles. The simulations were initialized at 400 K, so that both Ni and Al nanoparticles are solid at the start of the coalescence process. It is evident from Fig. 4 that the predicted adiabatic reaction temperature is in close agreement with the simulated temperature. The trend observed here is found to be similar to the results reported by Henz et al. (2009). This proves to be a strongly needed verification for our MD simulations. At the same time, it bolsters confidence in the thermodynamic model developed in this work.

The adiabatic temperature obtained from thermodynamic analysis and MD simulations is listed in Table 1. The reported temperatures suggest that the adiabatic reaction temperatures resulting from smaller particles tend to be greater than those obtained for the larger particles. This can be attributed to a higher reduction in surface energy (see Fig. 2) for smaller sized particles. This analysis and resulting formulation is the basis for our model predicting the dead layer thickness for the case of coated nanoparticles, as discussed later in Section Behavior of a single core-shell nanoparticle.

Now, in order to obtain the reaction time, the temperature variation graph generated through the MD simulation of the coalescence process is smoothed by the moving average method. To calculate the moving average, 600 points are taken into consideration.

The criterion temperature, which is defined as the temperature at which 95% of the difference between adiabatic reaction temperature and initiation temperature is achieved, is used. In this case (see Fig. 5), T_{ad} = 1905 K and thus the criterion temperature becomes 400+0.95*(1905-400) = 1829 K. Thus, the time corresponding to this temperature is the reaction time (16.575 ps in this case).

Figure 6 shows that the reaction time increases with the increasing particle size (volume to reaction surface area ratio). This trend can be attributed to two factors:

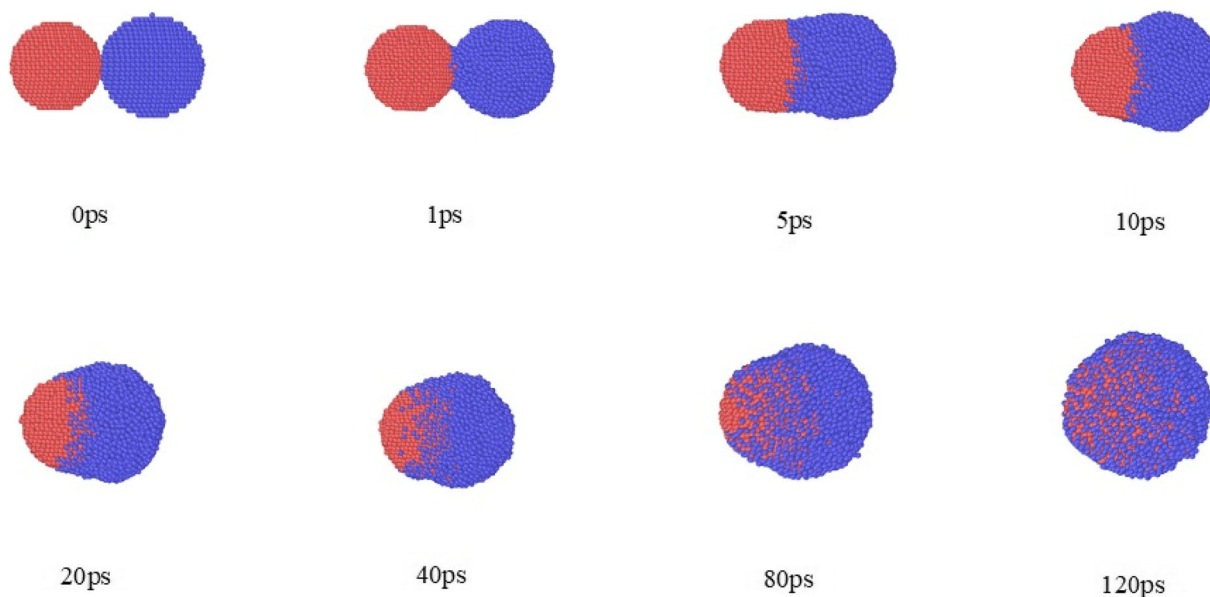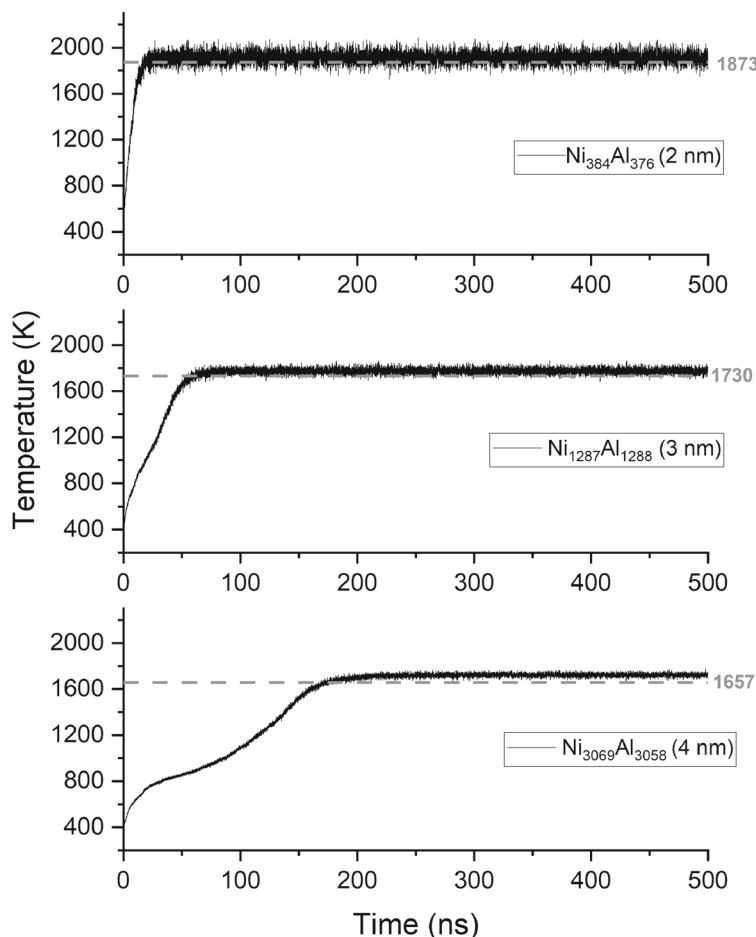1. For smaller particle size, the reaction temperature is higher due to higher reduction in surface energy/mol.

Fig. 3 MD simulation of coalescence of 4 nm Ni (red) and 4.596 nm Al (blue) nanoparticles

Fig. 4 Temperature vs time graph in the coalescence of Ni and Al nanoparticles in the molar ratio of 1:1. The predicted adiabatic reaction temperature through thermodynamic analysis is shown with dashed lines

2. The available reaction surface area/mol is also higher for smaller particles.

Therefore, reaction time $\tau_{reaction}$ is modeled to be inversely proportional to the specific reaction surface area of the particle:

$$\tau_{reaction} \propto \frac{1}{reaction\ surface\ area/mol} \qquad (16)$$

$$\tau_{reaction} \propto \frac{Total\ volume}{Surface\ area\ of\ Ni\ particle} \qquad (17)$$

$$\tau_{reaction} = c \times D + a \qquad (18)$$

Here, c is constant of proportionality, whose value is 234.1 ps/nm for the investigated cases, D is total volume (volume of Ni and Al) per unit reaction surface area of the system, and a is constant intercept. In this case of coalescence of Ni and Al nanoparticles, reaction surface area is the surface area of Ni particle

as the Al nanoparticle will melt and cover Ni particle to react (see Fig. 3).

Behavior of a single core-shell nanoparticle

In the coated nanoparticle system, core is composed of Al and shell is of Ni. The particle analyzed here contains the same number of Ni and Al atoms and hence the molar ratio of 1:1 is maintained (Fig. 7).

MD simulation results

The sintering of Ni-coated Al nanoparticle is simulated using LAMMPS (Plimpton 1995) and the system is initiated at 400 K. After the system is equilibrated at the temperature of 400 K, the constant energy NVE run is initiated and the simulation is then run for the desired time. The aforementioned simulation

Table 1 Comparison of adiabatic reaction temperature obtained from MD and the predicted temperature through the thermo dynamical analysis of system
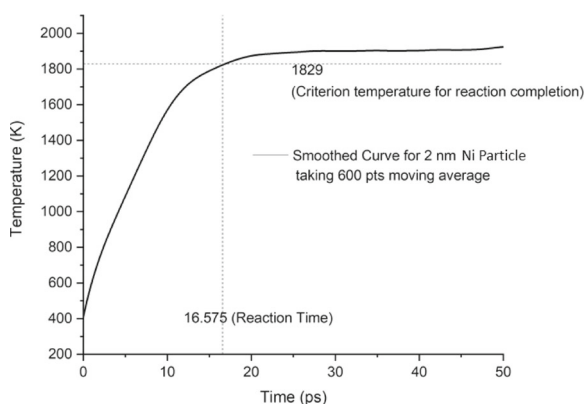
Ni diameter (nm)	Al diameter (nm)	T_{ad} (K) from thermodynamic model	T_{ad} (K) from MD	Change in surface energy(kJ/mole NiAl)	Reaction time (ps)
2	2.298	1873	1905	−28.576	16.575
3	3.447	1730	1775	−19.051	61.675
4	4.596	1657	1718	−14.288	188.95
Infinite	Infinite	1430	-	—	—

parameters are maintained for all the cases considered in the work and simulation time is varied depending on the cases considered. In this case, total simulation time is 300 ps. The molar ratio of Al and Ni has been kept 1:1.

The diameter of Al core considered in this study ranges from 4 to 6 nm. Figure 8 clearly shows that the time required for the completion of reaction increases with the increasing size of the nanoparticle. This is attributed to the higher reaction time for the bigger particles. The adiabatic reaction temperature obtained through the simulation is listed in Table 2.

The dead layer is the term given to the zone at the interface where it is proposed that the reaction between Ni and Al nanoparticles has already taken place. The atoms present in this region do not contribute to the rise of the temperature of the system. A model is developed to predict this dead layer thickness and it is discussed in the next section.

Table 2 shows that the adiabatic temperature increases only slightly with the decrease in particle size. This is attributed to the counteracting effects of a considerable reduction in specific surface energy and a significant increase in the fraction of reacted atoms at the interface of aluminum and nickel (see Table 3), with decrease in the particle size. The fraction of reacted atoms increased from 10.1% for 6 nm to 16.7% for 6 nm (see Table 3). Note that already reacted atoms present at the interface do not contribute to the rise of the temperature of the system.

Reaction time is plotted against ratio of volume to the reaction surface area for a better comparison with the subsequent cases. This ratio is directly proportional to the core diameter in this case. Hence, all results can be explained in terms of particle size too.

Figure 9 shows variation of reaction time with total volume per reaction area of the particle. In this case, the reaction area is the interfacial area between Al core and Ni shell. Reaction time again shows expected
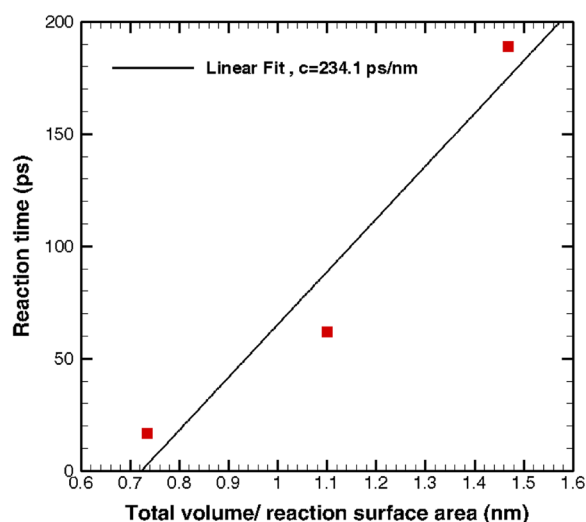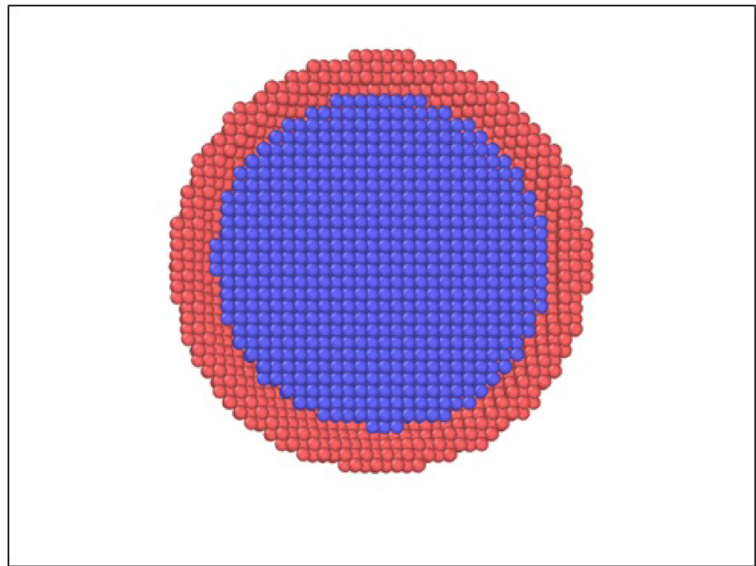

Fig. 5 Illustration of the process to obtain the reaction time for the coalescence process of Ni and Al nanoparticle (Ni = 2 nm, Al = 2.298 nm)

Fig. 6 Variation of reaction time with particle size

Fig. 7 Sectional view of Ni-coated Al nanoparticle

trends as it increases with the increasing particle size (volume to reaction surface area ratio). The trend is similar to the trend obtained for separate Ni and Al nanoparticle coalescence, as shown in Fig. 6. The reaction time is different as the configuration of the nanoparticle is considerably different in this case. The value of constant of proportionality c is 133.26 ps/nm (see Eq.18), which is less compared with c obtained in the previous case of separate Al and Ni nanoparticles (234.1 ps/nm).

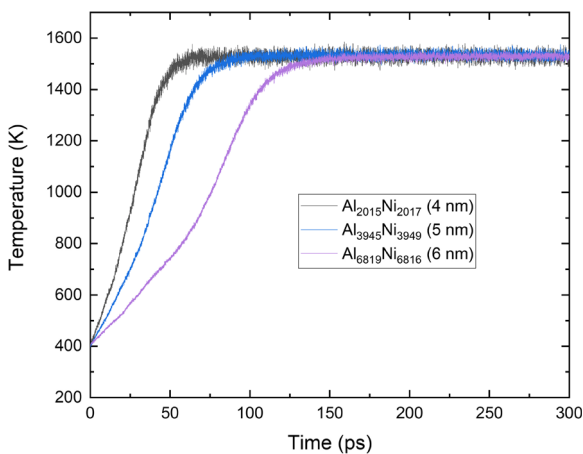The Ni particles are present around the Al core and thus the contact time between Ni and Al is comparatively much faster in this case compared with the separate nanoparticle case and that is reflected in lower c. The simulation process is visualized in OVITO (Stukowski 2010) and the resulting images have been shown in Fig. 10. The gradual changes in the structure can be observed to a certain extent in these images.

Thermodynamic analysis

The thermodynamic analysis of Ni-coated Al nanoparticle is similar to the analysis carried out in the previous section for separate Ni and Al nanoparticles, accounting for the dead layer thickness. The equations that will again be followed here are as follows:

$$H_{reactants} = H_{products} \tag{19}$$

Model to predict dead layer thickness

The "dead layer model" accounts for the existence of a dead layer of finite thickness in computation of the adiabatic reaction temperature. The energy release, which causes the temperature of the system to rise, has two main components, namely change in surface energy and heat release due to the intermetallic reaction between Ni and Al. It is assumed that when the Ni and Al come in contact in the interfacial region, they form Ni–Al bond, which results in a fraction of Ni and Al atoms already at a lower configurational

Fig. 8 Time evolution of temperature during the coalescence of single core-shell nanoparticles

Table 2 Adiabatic reaction temperature of Ni-coated Al nanoparticle predicted through thermodynamic analysis

Al core dia (nm)	Ni shell dia (nm)	T_{ad} (K) from MD	Change in surface energy (kJ/mole NiAl)	Reaction time (ps)
4	4.735	1548	−27.132	60.75
5	5.919	1540	−21.706	88.23
6	7.103	1530	−18.733	143.40

energy, which in turn results in a lower adiabatic reaction temperature. So, in a sense, there is some NiAl already formed before the constant energy run begins.

Let the fraction that has already reacted to be given as $f = 1 - x$, which implies:

$$x Ni + x Al + f NiAl \rightarrow NiAl \qquad (20)$$

Thermodynamic analysis for reactants results in:

$$H_{reactants} = x \left(H_{Al,400K} + H_{Ni,400K} \right) + H_{Ni,surf} + f H_{NiAl,400K} \qquad (21)$$

where molar enthalpy, $\overline{h}_{NiAl,400K}(T)$ is given as:

$$\overline{h}_{NiAl,400K}(T) = \overline{h}^{\circ}_{NiAl,form,298K} + \int_{298}^{400} c_p(T)\, dT \qquad (22)$$

The enthalpy of products for the prediction of adiabatic reaction temperature is same as formulated in previous section Eq. 8 and molar enthalpy, $\overline{h}_{NiAl,T_{ad}}(T)$, is same as Eq. 9.

The fractions of Ni and Al atoms that have already reacted are calculated by inserting the T_{ad} values obtained from MD simulation of sintering of Ni-coated Al nanoparticles (see Table 2). Since T_{ad} is known, the only unknown remaining is the fraction

of nanoparticle that has already reacted (f) and the calculated values are listed in Table 3.

It is observed that the reacted fraction shows a decreasing trend with increasing size of the nanoparticle, but this does not give a clear idea of the dead layer thickness. This fraction is further utilized to find the thickness of the dead layer. Figure 11 shows the sectional view of Ni-coated Al nanoparticle, depicting the dead layer thickness. A unitary method is applied to find the number of atoms which have already reacted in order to find the volume of the reacted part. The total number of atoms of Ni and Al is already known and hence the fraction of atoms reacted can be calculated. Firstly, the number of atoms reacted of each Ni and Al is found and then the mass of these atoms is found. The volume of the reacted fraction is calculated separately using the densities of Ni and Al. The total volume already reacted of Ni and Al together gives us the total volume of the dead layer. The numbers of reacted atoms are the same for both Ni and Al, as it is assumed that the formation of NiAl presents the requirement of the Ni and Al atoms in the atomic ratio of 1:1.

The reacted volume is used to predict the dead layer thickness. To calculate the dead layer thickness, it is assumed that the reacted portion of Ni and Al does not experience any diffusion and the dead layer comprises of two sub dead layers entirely made up of the same element. In other words, the formed NiAl as a

Table 3 Dead layer thickness calculated for Ni-coated Al nanoparticles

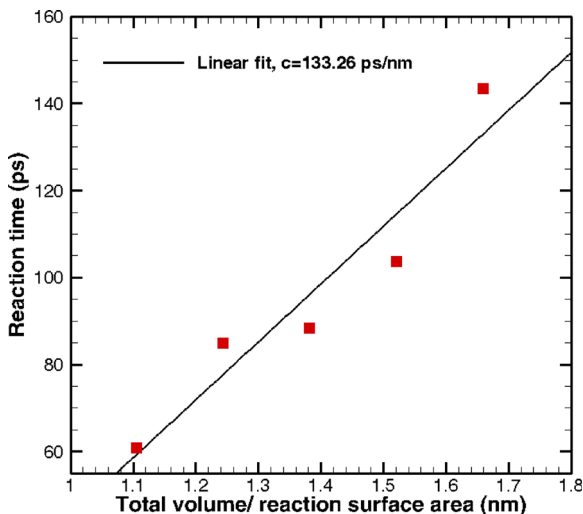| Al core diameter (nm)	Ni shell diameter (nm)	Reacted thickness$_{Al}$ (nm)	Reacted thickness$_{Ni}$ (nm)	Reacted fraction (f)	Dead layer thickness (nm)
4	4.735	0.1179	0.0707	0.167	0.1886
5	5.919	0.1091	0.0670	0.125	0.1761
6	7.103	0.1042	0.0650	0.101	0.1692

Fig. 9 Variation of reaction time with total volume/reaction surface area of single core-shell nanoparticles

result of reaction between Ni and Al atoms completely occupies the space vacated by Ni and Al atoms that have reacted, which implies that:

$$Volume\ of\ Al\ reacted = \int_{r_{Al}}^{R_i} 4\pi r^2\ dr \qquad (23)$$

where R_i represents the core radius, as shown in Fig. 11. The thickness of Al reacted is given by:

$$Reacted\ thickness_{Al} = R_i - r_{Al} \qquad (24)$$

Similarly, reacted thickness of Ni is estimated as follows:

$$Volume\ of\ Ni\ reacted = \int_{R_i}^{r_{Ni}} 4\pi r^2\ dr \qquad (25)$$

$$Reacted\ thickness_{Ni} = r_{Ni} - R_i \qquad (26)$$

The thickness of the dead layer can be obtained by the addition of reacted thickness of Ni and Al. The results from the above calculations are tabulated in Table 3. Dead layer thickness varies between 0.17 and 0.19 nm for the nanoparticle core radius ranging from 4 to 6 nm. The dead layer thickness does not change significantly with the size of the nanoparticle and it is found to be $\sim$ 0.18 nm. Since the diameter of aluminum atom is $\sim$ 0.18 nm and the diameter of nickel atom is $\sim$ 0.16 nm, it seemingly appears that the already reacted part or dead layer is a single atom layer wherein the reacted atoms of nickel and aluminum lie in a single layer. Hence, it seems that the dead layer is a local phenomenon rather than global. Though the dead layer thickness does not change significantly,
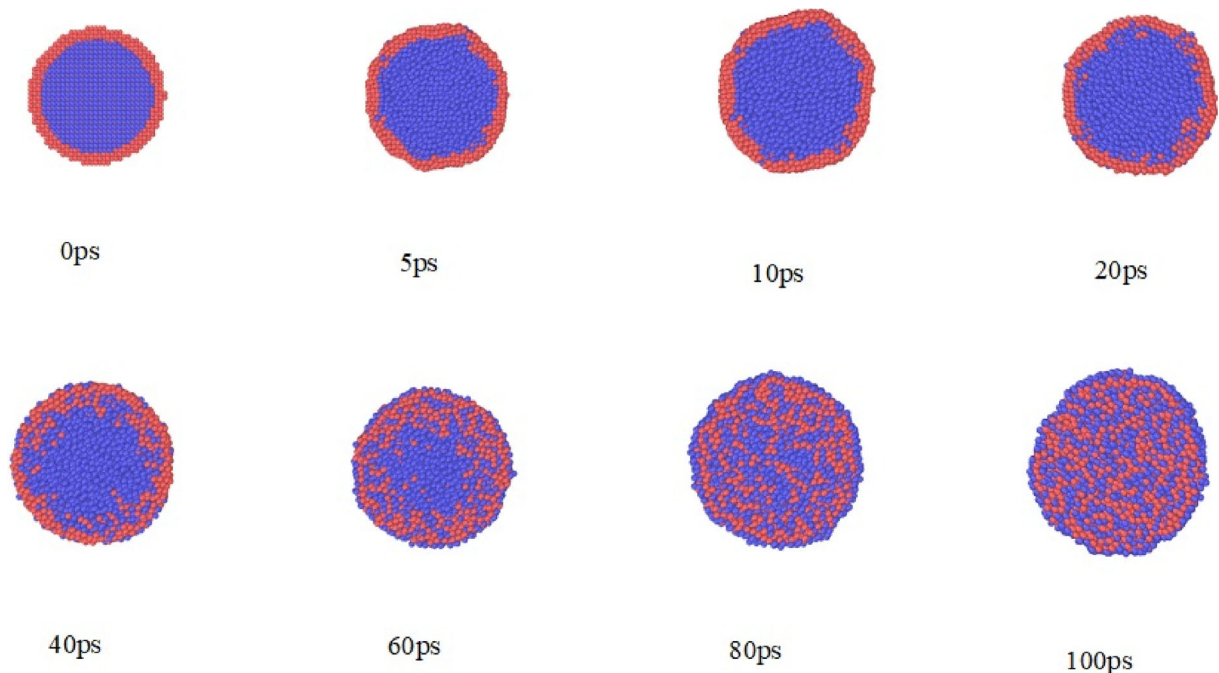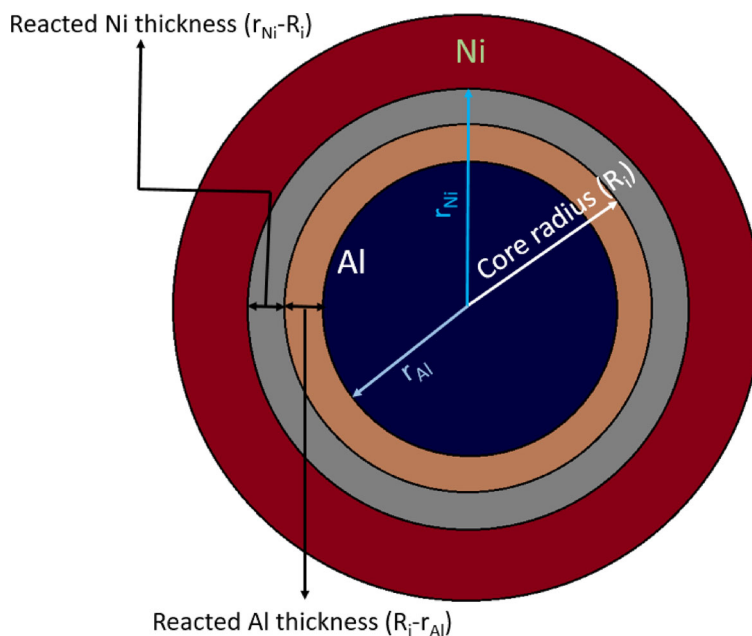

Fig. 10 MD simulation of sintering of Ni (Red) coated 5 nm Al (Blue) nanoparticle

Fig. 11 Sectional view of
Ni-coated Al nanoparticle

Reacted Ni thickness ($r_{Ni}-R_i$)

Ni

r_{Ni}

Al

Core radius (R_i)

r_{Al}

Reacted Al thickness (R_i-r_{Al})

the fraction of already reacted atoms increases con-
siderably with a decrease in the particle size. This
would tend to decrease the adiabatic reaction tempera-
ture. The concept of dead layer thickness is introduced
to segregate/visualize these reacted atoms. The thick-
ness is just an indication and does not imply that
the already reacted atoms must form a circular ring.
The reacted atoms may be unevenly distributed. These
results can thus be utilized to develop a model to pre-
dict adiabatic reaction temperature of Ni-coated Al
nanoparticles. The model is then used to predict the
adiabatic reaction temperature for the coalescence of
coated nanoparticles, as discussed in the next section.

Coalescence of two separate core-shell nanoparticles

In this section, the model used for predicting the
dead layer thickness is utilized to predict the adiabatic
reaction temperature for the coalescence of two Ni-
coated Al nanoparticles. This, in a way, also serves
as a validation of the model that is used to predict
the dead layer thickness. Thermodynamic analysis
and MD simulations of coalescence have been done
for both equal-sized and different-sized Ni-coated Al

nanoparticles. In the case of coalescence process of
equal-sized particles, particles of core diameters 4 nm,
5 nm, and 6 nm are made to coalesce with same con-
figuration diameter. For unequally sized particles, a
few different combinations are taken into considera-
tion. The key point to note here is that the atomic ratio
of Al and Ni in all the combinations remains 1:1.

Coalescence of two Ni-coated Al nanoparticles

The analyses are done for the particles having core
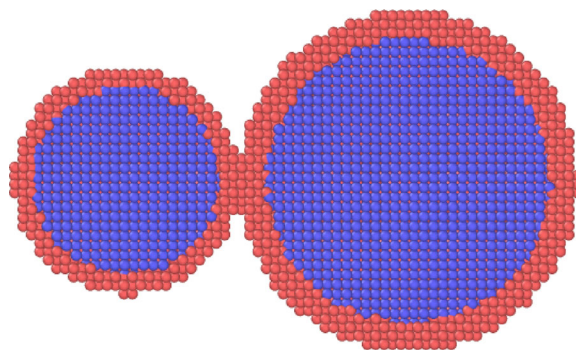diameter ranging from 4 to 6 nm (Fig. 12).

Fig. 12 Sectional view of two unequally sized Ni-coated Al
nanoparticles

Thermodynamic analysis

The thermodynamic analysis of these particles is similar to the coalescence of separate nanoparticles with the dead layer thickness taken into account. Therefore, all the equations followed in this case are the same as discussed in the previous section. The representative equation for the coalescence of two Ni-coated Al nanoparticles is given as:

$$x_1 Ni + x_1 Al + x_2 Ni + x_2 Al + f_1 NiAl + f_2 NiAl \rightarrow 2NiAl \tag{27}$$
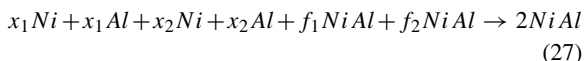
where $x_1 + f_1 = 1$ and $x_2 + f_2 = 1$

The values of a reacted fraction are taken from Table 3. The product side remains the same with just the multiplication by a factor of 2, but the reactant side becomes:

$$H_{reactants} = (x_1 + x_2)\left(H_{Al,400K} + H_{Ni,400K}\right) + 2H_{Ni,surf} + (f_1 + f_2)H_{NiAl,400K} \tag{28}$$

The predicted adiabatic reaction temperature in Table 4 shows a decreasing temperature as the size of the particles increases. This is attributed to the change in the surface energy of these particles. The variation in temperature is very much similar to the variation of change in surface energy in terms of magnitude.

MD simulation results

The coalescence of two Ni-coated Al nanoparticles is simulated through LAMMPS (Plimpton 1995). The smallest nanoparticle in this analysis has a core diameter of 4 nm and the largest one has a core diameter of 6 nm. The OVITO visualization of the coalescence of two unequally coated nanoparticles is depicted in Fig. 13.

Figure 14 shows that the coalescence of bigger particles takes a longer time to get completed which is intuitively the correct trend. The final adiabatic reaction temperature in coalescence of two Ni-coated Al nanoparticles is slightly above the temperature resulting from sintering of a single Ni-coated Al nanoparticle and the reason behind it is higher reduction in specific surface energy for separate particles.

Figure 15 shows the variation of reaction time with the effective size (in terms of the ratio of the total volume of the two coalescing nanoparticles to their

Table 4 Adiabatic reaction temperature obtained from MD simulations and the predicted temperature for coalescence of two separate Ni-coated Al nanoparticles

| Al core dia 1 (nm)	Al core dia 2 (nm)	Dead layer thickness 1 (nm)	Dead layer thickness 2 (nm)	Change in surface energy (kJ/mole NiAl)	T_{ad} predicted (K)	T_{ad} from MD	T_{ad} single core-shell MD	Reaction time (ps)
4	4	0.1886	0.1886	-32.68	1635	1615	1548	54.92
4	5	0.1886	0.1761	-28.14	1602	1597	-	74.25
5	5	0.1761	0.1761	-25.15	1609	1600	1540	92.73
4	6	0.1886	0.1692	-23.69	1556	1579	-	98.56
5	6	0.1761	0.1692	-23.26	1587	1590	-	106.10
6	6	0.1692	0.1692	-21.79	1587	1583	1530	138.43
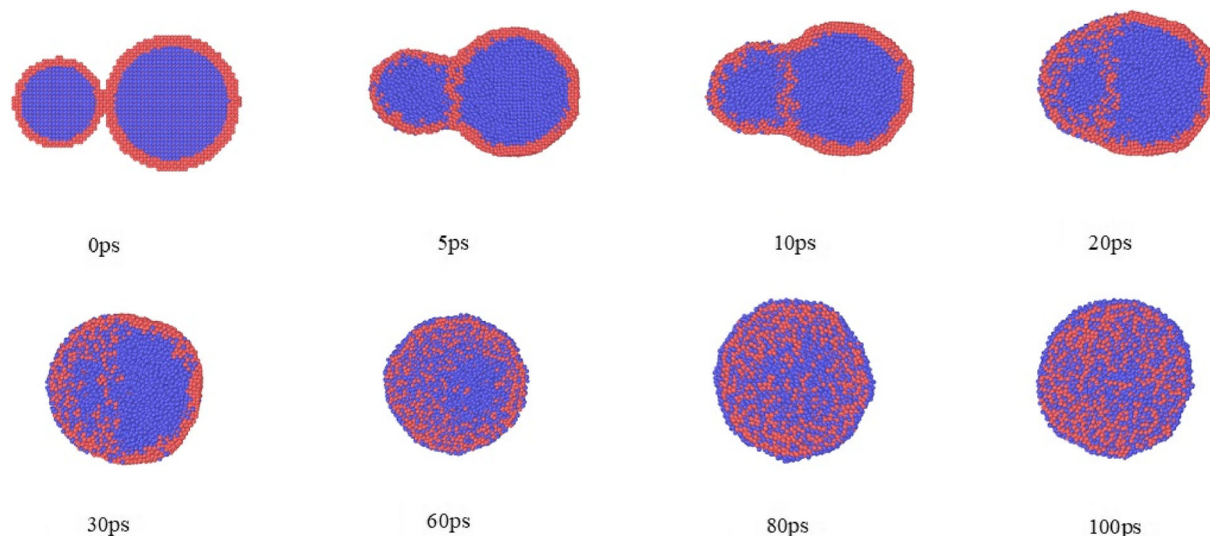
Fig. 13 MD simulation of coalescence of two unequally sized Ni (red) coated Al (blue) nanoparticles

total reaction surface area) of two particles. In this case, also the reaction surface area is the interfacial area between the core and shell. The constant of proportionality c is found to be 138.72 ps/nm, which is slightly higher than the c in the case of single core-shell particle (133.26 ps/nm).

Figure 16 shows the variation of reaction time with total volume/reaction surface area for different cases discussed in this work. It gives a better comparative understanding of the effect of different cases on reaction time with particle size. The constant of proportionality c or the slope of linear fit is found to be maximum for coalescence of separate Al and Ni
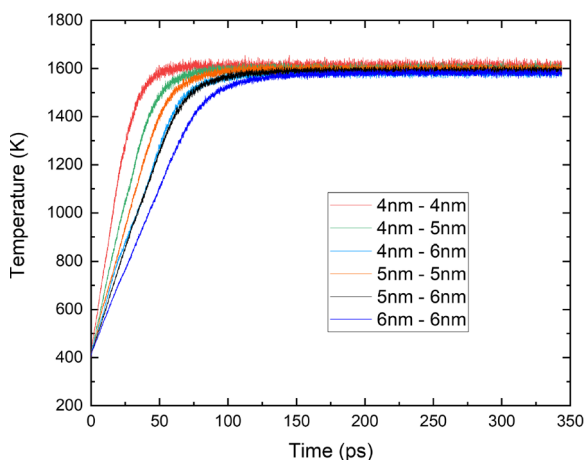
nanoparticles, while minimum for the single core-shell particles. The reaction time of separate core-shell particles is almost similar compared with the single core-shell particles (see Tables 2 and 4). The reaction time of separate nanoparticles is higher than the core-shell particles because in the former case, a separation distance is being maintained between the reactants at the initiation of the reaction whereas in the latter the reactants are in close contact at the interface. The precise parameter for consideration here is however the total volume to reaction surface area ratio,
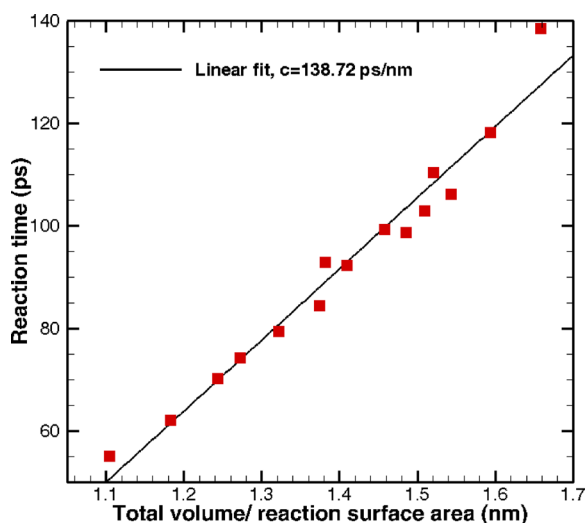

Fig. 14 Time evolution of temperature during the coalescence of two separate core-shell nanoparticles

Fig. 15 Variation of reaction time with total volume/reaction surface area ratio of two core-shell nanoparticles
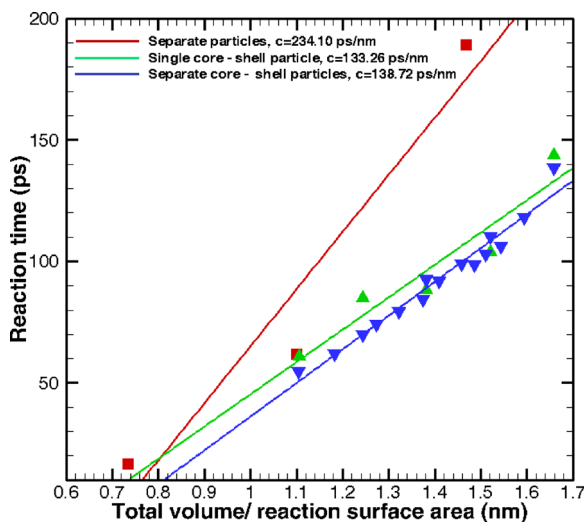
Fig. 16 Variation of reaction time with total volume/reaction surface area ratio for different cases

which is also an indicator of the size of the interacting nanoparticles.

Conclusions

The present study aimed to develop a thermodynamic model to accurately predict the adiabatic reaction temperature of Ni-coated Al nanoparticles. The first part of the work discussed an in-depth and thorough thermodynamic analysis of the coalescence process of separate Ni and Al nanoparticles. In the second part, a model was developed to calculate the dead layer thickness utilizing the results from MD simulations for single Ni-coated Al nanoparticles. In the final part, the model incorporating the dead layer thickness was put to the test by analyzing the coalescence of separate Ni-coated Al nanoparticles. Coalescence of both equally and unequally sized nanoparticles was considered for these analyses. The model was found to be effective in predicting the adiabatic reaction temperature of the system. The results obtained from the MD simulations of the coalescence of separate Ni-coated Al nanoparticle were in good agreement with the predicted temperatures. The key conclusions from the present study of coalescence of Ni-coated Al nanoparticles are listed here:

- The variation of adiabatic reaction temperature was found to be primarily governed by reduction in surface energy and already reacted fraction. The adiabatic reaction temperature was higher for a larger decrease in surface energy per unit mole of NiAl and lower fraction of reacted atoms.

- Dead layer thickness, calculated for the Ni-coated Al nanoparticles of core diameter ranging from 4 to 6 nm, was found to be in the range of 0.17 to 0.19 nm. The thickness calculated from the reacted fraction was found to depend weakly on the size of the particle.

- The prediction of adiabatic reaction temperature of coalescence of two separate Ni-coated Al nanoparticles accounting for the dead layer thickness was found to be accurate and was verified by the results from MD simulations.

- Reaction time was found to vary inversely with reaction surface area per mole. The coalescence and energetic reactions for larger particles were observed to take a longer time to get completed.

- Construction of initial configuration, especially for coated nanoparticles, is a challenging task. In the future, an improved approach can be pursued to build a more accurate initial configuration.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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