The size and temperature effect on titanium Ti_7 cluster in β-$TiCl_3$ medium

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Abstract. In the Kroll process, the reduction process results in the production of intermediates such as titanium trichloride ($TiCl_3$) and titanium dichloride ($TiCl_2$). There has been experimental work on developing a continuous reduction process using $TiCl_3$ and $TiCl_2$. However, more investigations still need to be done to understand these mediums and their interactions. In this paper, we will be investigating one $TiCl_3$ polymorph as a potential medium for titanium production. We employ the DL_POLY code to understand the effect of temperature on the Ti_7 cluster using a stable β-$TiCl_3$ medium. It was observed from the total energies that the system is stable at 50 – 700 K. The diffusion coefficient results showed that the Ti_7 nanocluster diffuses faster than Ti and Cl at 1300 – 2000 K.

1 Introduction

The excellent properties of titanium, such as its high strength-weight ratio and low density, make it ideal for use in aerospace and other industries [1,2]. As such, the demand for titanium increases every year [2]. To date, the Kroll process is exclusively used worldwide in the commercial production of titanium sponge [3]. During this magnesiothermic reduction of titanium tetrachloride ($TiCl_4$), intermediate products titanium trichloride ($TiCl_3$) and titanium dichloride ($TiCl_2$) are also obtained in this process [2]. However, the reduction process is fast and results in the formed titanium deposits firmly adhering to the reactor [4]. Thus, compromising the quantity of titanium. The Kroll process has undergone constant development since it was first introduced, resulting in increased output and energy efficiency [5].

In-depth research studies and process improvements have been made in an effort to address some of the shortcomings of the Kroll process. These initiatives aim to create a continuous production process to reduce the cost of titanium metal production [5]. One proposed initiative is the production of titanium through the magnesiothermic reduction of $TiCl_3$. This proposed process is advantageous since it is possible to make the process eco-friendly by using titanium scraps. Although some effort has been made experimentally, there are some challenges still encountered such as blockage of the magnesium supply pathway resulting in an incomplete reduction process [6].

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In this study, a molecular dynamic approach is employed to understand the titanium production process in particular, to investigate $TiCl_3$ as a possible medium for the production of titanium. We first report on the bond length of the Ti_7 nanocluster after interactions with the β-$TiCl_3$ medium; secondly, the energy dependence at various temperatures and diffusion coefficient of the β-$TiCl_3$/Ti_7 system are discussed.

2 Methodology

The Ti_7 nanocluster was developed using the Knowledge-Led Master Code (KLMC) [7] employing the genetic algorithm module. This code has been proven to accurately locate local and global minima on the potential energy surface so as to predict the structure of metallic clusters or their alloys. The Ti_7 nanocluster was then validated using the General Utility Lattice Program (GULP) [8], which is used to perform various simulations on materials employing boundary conditions unique to the type of material.

Classical molecular dynamics simulations were performed using the DL_POLY code [9]. This code is ideal for simulating large systems and for understanding the reactivity, and structure of materials. A radial cut-off of 9.95 Å was used in a simulation of 5839 atoms of β-$TiCl_3$/Ti_7 system with β-$TiCl_3$ having a $P6_3$/mcm space group. An NVT ensemble employing the Nosé-Hoover thermostat and barostat was run for 50000 steps to bring the system to equilibrium. Furthermore, the time step was set at 1e-6 ns employing a simulation time of 200 ps while increasing the temperature from 50 to 2000 K.

3 Results and discussion

In this section, we give insights into the size of the nanocluster after interactions with the β-$TiCl_3$ medium. The total energy and diffusion coefficient were also investigated for the β-$TiCl_3$/Ti_7 system. Firstly, we monitor the effect of β-$TiCl_3$ medium on the physical and thermodynamic properties of the Ti_7 nanocluster as the temperature is increased. Secondly, the energy dependence at various temperatures of the system is investigated to understand the effects of temperature on the stability of the system. Finally, the diffusion coefficient (DC) is used to trace the trajectories of Ti, Cl and Ti_7 in the system and to understand the motion of these ions.

3.1 Effect of β-$TiCl_3$ medium on the Ti_7 nanocluster

Figure 1 shows the Ti_7 nanocluster with the A, B, C, D bond sites. The A-B bond sites denotes the bond between A and B at an obtuse angle on the cluster. A B-C bond site is a forward inclined bond between B and C. The bond connecting A and C that inclined slightly down the front of the Ti_7 nanocluster is noted as the A-C bond site. The bond connecting A and D inclined slightly down the back of the Ti_7 nanocluster is noted as the A-D bond site. The bond between B and D that rises at the cluster's rear is noted as the B-D bond site. The C-D bond spans C and D at the cluster's centre and is noted as the C-D bond. Figure 2 shows the Ti-Ti bond distances for the Ti_7 nanocluster in vacuum and β-$TiCl_3$ medium at different temperatures. This was to investigate how β-$TiCl_3$ may influence the physical and thermodynamic properties of Ti_7 as the temperature is increased.

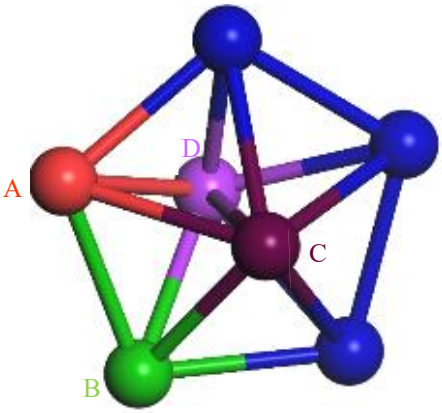

Fig. 1. Snapshot of the Ti_7 nanocluster in its stable pentagonal bipyramid geometry.

Figure 2a shows the Ti-Ti bond lengths of the nanocluster in vacuum. We note that the Ti-Ti bond length shrinks from $b_{i(A-B)} = 2.754$ Å (low temperature, 300 K) to $b_{f(A-B)} = 2.698$ Å (at 1100 K). A similar shrinking-elongation trend is observed across all bond sites as temperature is increased. The B-C and C-D bond length sharply increase at 1100 K suggesting that the bonds are weaker at that temperature.

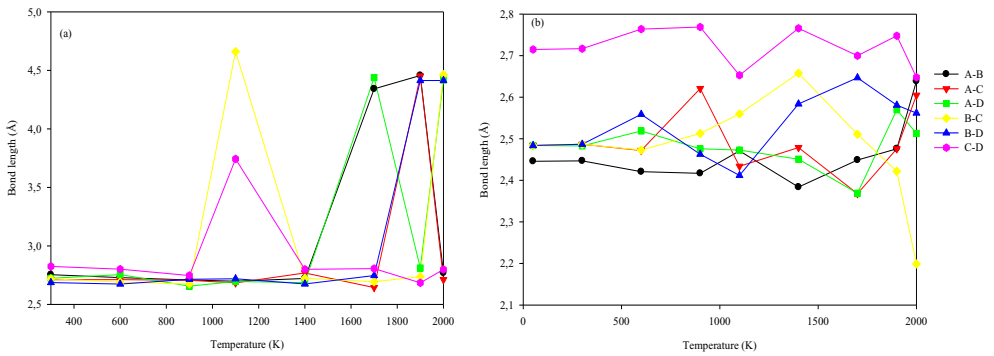

Fig. 2. Ti-Ti bond length of Ti_7 nanocluster in (a) vacuum and (b) β-$TiCl_3$ medium.

However, in the presence of β-$TiCl_3$ medium (figure 2b), we note that there is an elongation of Ti-Ti bonds from $b_{i(A-B)} = 2.446$ Å (low temperature, 50 K) to $b_{f(A-B)} = 2.447$ Å (300 K). We also note that the bond increases at high temperatures at $b_{i(A-B)} = 2.384$ Å to $b_{f(A-B)} = 2.639$ Å at 1400 K – 2000 K. At 1100 K, the bond length shrinks along C-D and B-D, suggesting that the bonds are stronger compared to Ti_7 nanocluster in vacuum. In addition, the Ti-Ti bond lengths of the Ti_7 nanocluster in the medium are shorter compared to the Ti_7 nanocluster in vacuum. This observation suggests that the structure size and stability is preserved in the β-$TiCl_3$ medium. Interestingly, B-C and B-D collapses near the melting temperature of Ti (1915 K) at 1400 – 2000 K, and 1700 – 2000 K, respectively. This suggests that the nanocluster is more preserved in the medium than in vacuum.

3.2 Energy dependence at various temperatures

Figure 3 illustrates the total energy of the Ti_7 nanocluster, β-$TiCl_3$ and β-$TiCl_3$/Ti_7 systems at different temperatures. In order to analyse the behaviour of the mediums, the energies were normalized. The graph shows a constant linear increase in energy with an increase in temperature. This implies that the kinetic energy of the system also increases as a result of the increasing movement of molecules in the system. We note that the Ti_7 nanocluster is stable, indicated by the negative total energy values. The plot also shows similar total energy values at 300 -1100 K and 1915 – 2000 K.

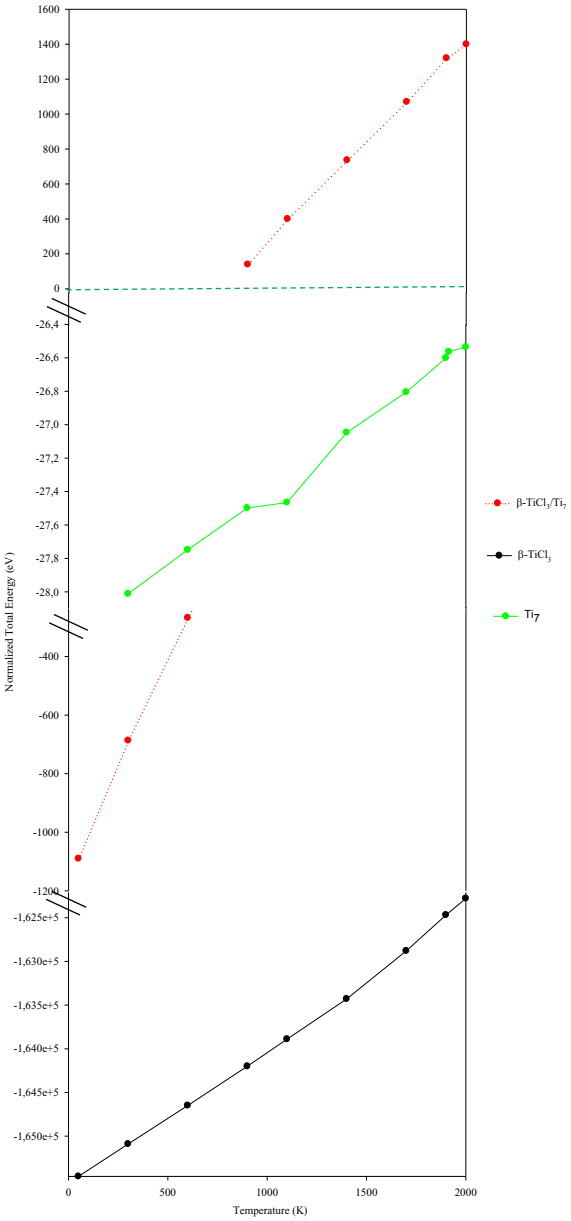

Fig. 3. Total energy of the Ti_7 nanocluster, β-$TiCl_3$ and β-$TiCl_3$/Ti_7 system at different temperatures.

This suggests a possible change in the geometry of the cluster from a stable pentagonal bipyramid geometry to unstable capped octahedron geometry. Both β-$TiCl_3$ and β-$TiCl_3$/Ti_7 systems do not show an obvious phase transition from 50 – 2000 K. We note that for the β-$TiCl_3$ medium, the total energy values are negative i.e., $E_{tot} < 0$, at 50 – 2000 K. This is an indication that the β-$TiCl_3$ medium is more favourable at that temperature range. Thus, indicating stability of the medium at 50 – 2000 K. We further note that for β-$TiCl_3$/Ti_7 system, the reactions are favourable at 50 – 700 K. It can be deduced that the medium decreases the stability of the cluster to 50 – 700 K. At 800 – 2000 K, the total energy values are positive which suggests that the system is unfavourable. However, the recommended temperature range to be maintained for $TiCl_4$ medium, is 1093 – 1123 K in order to produce quality titanium components [10]. The current predicted 700 K for β-$TiCl_3$ medium which showed decreased stability suggesting that the reduction of titanium took place. It should be noted that these results are for β-$TiCl_3$ medium. The observations suggest that the β-$TiCl_3$ medium can be used in enhancing titanium products at lower temperatures compared to $TiCl_4$.

3.3 Diffusion coefficient

Figure 4 shows the diffusion coefficient (DC) plot for the β-$TiCl_3$/Ti_7 system. The DC rate of Ti, Cl and Ti_7 was compared as a function of temperature. More interestingly, we note that the Ti_7 curve shows an exponential increase in the DC rate as temperature increases. In addition, Ti and Cl in the system depict a linear increase in diffusivity.

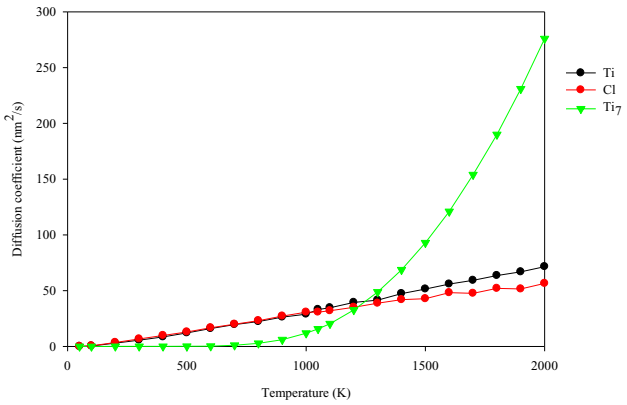

Fig. 4. Diffusion coefficient for Ti, Cl and Ti_7 ions in the β-$TiCl_3$/Ti_7 system.

The diffusion coefficient for Ti and Cl revealed similar temperature agitation at 50 – 1100 K. At 1200 – 2000 K, Ti is observed to have higher diffusivity than Cl. For the Ti_7 nanocluster, the diffusivity is observed to be zero at 50 – 700 K. However, as the temperature increases from 800 – 2000 K, the diffusivity increases exponentially. These observations are similar to the total energy results (figure 3), where we observed the decrease in the stability of the cluster at 800 – 2000 K. This might be attributed to the molecular weight of the nanocluster being lighter compared to Ti and Cl. Furthermore, the observation indicates that Ti_7 is the main diffusion species in the β-$TiCl_3$/Ti_7 system and has very low solubility.

4 Conclusion

We investigated the effect of β-$TiCl_3$ on the Ti_7 titanium nanocluster at different temperatures. Molecular dynamics results showed that the Ti-Ti bond lengths of the Ti_7 nanocluster are stronger in the medium than in vacuum. The observation suggested that the nanocluster is preserved in the medium. It was noted from the energy dependence results that the β-$TiCl_3$/Ti_7 system is stable at 50 – 700 K and that the β-$TiCl_3$ medium destabilises the cluster above 700 K. Furthermore, the diffusion coefficient graph showed that Ti_7 diffuses faster than Ti and Cl at 1300 – 2000 K. Furthermore, the findings indicate that β-$TiCl_3$ is a favourable medium for reducing titanium at low temperatures < 800 K.

Acknowledgements

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