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Modelling of Ti and Cl diffusivity in two $TiCl_4$ mediums for titanium production processes

Andile Mazibuko[1*], *Phuti* Ngoepe[1], and *Hasani* Chauke[1]

[1]Materials Modelling Centre, University of Limpopo, Private Bag X1106, Sovenga, 0727, South Africa

Abstract. Titanium, a metal highly valued for its outstanding properties, is in increasing demand. The primary method for its production involves reducing titanium tetrachloride ($TiCl_4$) with magnesium (Mg). However, this process is conducted batch-wise, making the development of a continuous reduction process challenging. Developing continuous reduction processes requires a detailed understanding of $TiCl_4$ behaviour, including diffusion and thermodynamic stability. Past modelling efforts have not provided an in-depth understanding of the diffusion behaviour of $TiCl_4$. While $TiCl_4$ has been studied computationally in ionic liquid systems, detailed atomistic insights remain limited. In this study, we employed the classical molecular dynamics DL_POLY code to investigate temperature effect on titanium (Ti) and chlorine (Cl) diffusion in the $TiCl_4$ medium. Analysis of the diffusion coefficients revealed a linear trend in the diffusion of Ti and Cl ions in the $P12_1/c$ structure from 50 K to 2000 K, consistent with expected thermodynamic behaviour. These results shed light on how structural differences in $TiCl_4$ influence ion mobility and stability, which can support accurate modelling of mass transport in $TiCl_4$ under process-relevant conditions. Moreover, the findings provide valuable insights that can inform future refinements in titanium production processes.

1 Introduction

Titanium is valued for its superior corrosion resistance, biocompatibility and low density [1]. The metal is primarily extracted from mineral sands, and South Africa is one of the top producers of titanium-bearing minerals worldwide [2]. Titanium alloys, for instance, are used in the aerospace industry to manufacture aeroplane components, significantly improving performance and fuel efficiency [1,3]. The automotive industry also benefits from the high strength-to-weight ratio of titanium in producing high-performance parts. Additionally, titanium is useful for prosthetics and medical implants due to its biocompatibility [1,3].

The predominant method for the commercial production of titanium is the magnesiothermic reduction of titanium tetrachloride ($TiCl_4$); however, this process has notable limitations, primarily due to its batch-wise nature [4,5]. Understanding the $TiCl_4$ medium is essential for producing high-quality titanium with reduced environmental impact. The purity of titanium is crucial in aerospace and medical devices, with high-performance

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[*] Corresponding author: andileZibu@gmail.com

criteria [6]. However, there is limited information on the modelling of $TiCl_4$. Recent research has investigated the interaction of $TiCl_4$ in ionic liquid mixtures [7]. It was found that water (H_2O) and $TiCl_4$ compete to interact primarily with Cl^- and they also interact with each other, significantly affecting cation-anion interaction. This can enhance the cation-anion interactions in certain systems [7].

This study aims to explore the molecular dynamics properties in the titanium production process, providing crucial insights into how temperature affects liquid $TiCl_4$ medium. We employed classical molecular dynamics to investigate the behaviour of atoms in a liquid $TiCl_4$ medium. We intend to enhance the understanding of the process significantly. In particular, we report on the effects of temperature variations on the atomic behaviour in $TiCl_4$. Section 2 outlines the methodology, and Section 3 discusses the effect of temperature on the diffusion coefficients of Ti and Cl ions, as well as the stability of the medium through the total internal energy. The conclusion is provided in Section 4.

2 Methodology

We employed classical molecular dynamics to investigate the thermodynamic properties of the titanium tetrachloride ($TiCl_4$) medium with $P12_1/c$ and $P2_1/c$ space groups. The $TiCl_4$ medium was developed and validated using the general utility lattice program (GULP) [8], which is useful for developing materials with specific properties. Temperature dependence calculations were performed using the DL_POLY code [9,10], suitable for large-scale simulations and studying complex systems. This code will help predict how titanium atoms interact at a molecular level and identify energy-efficient pathways for titanium production. Interactions between Ti-Ti and Cl-Cl were described using Buckingham interatomic potential parameters from the CATLOW library. Interatomic potentials for Ti-Cl interaction were derived in a previous study and fine-tuned to the $TiCl_4$ medium [11]. The $P12_1/c$ and $P2_1/c$ structures were simulated using a radial cut-off of 9.95 Å. Additionally, the simulation time was set to 10 ns with a time step of 0.001 ps, and the temperature was varied from 50 K to 2000 K in NVE microcanonical ensemble. This broad temperature range is needed to thoroughly understand the temperature dependent behaviour of $TiCl_4$ interactions with Ti nanoclusters. The two crystal structures are shown in figure 1.

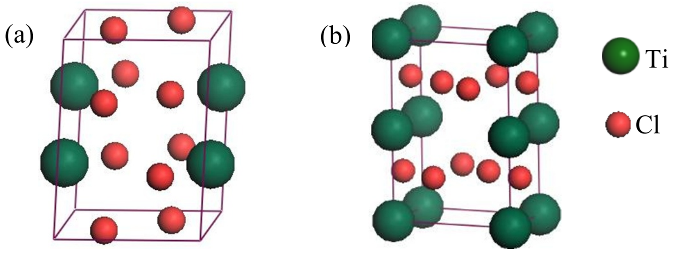

Fig. 1. Atomic arrangement of the (a) $P12_1/c$ and (b) $P2_1/c$ crystal modifications of $TiCl_4$ medium.

3 Results and discussion

3.1 Structure validation

We performed constant-temperature and pressure optimisation using the GULP code to minimise the total energy of the system and obtain equilibrium structural properties. This confirmed that the selected Buckingham interatomic potentials from the Catlow library and the fine-tuned Ti-Cl Morse potentials were valid for the TiCl$_4$ models. Validation was done by comparing the experimental (Exp.) lattice parameters versus those derived from the simulation run (Calc.). The results are shown in Table 1.

Table 1. The calculated (Calc.) and experimental (Exp.) lattice parameters and bond lengths of the crystal modifications of TiCl$_4$.

Structure	Lattice parameters				Ti-Cl bond length (Å)	
	a (Å)	b (Å)	c (Å)	Volume (Å^3)	Calc.	Exp.
$P12_1/c$ Calc.	9.142	4.165	9.719	292,876	2.168	2.170 [13]
Exp.(a)	9.670	6.474	9.682	592.412		
$P2_1/c$ Calc.	8.865	4.432	8.776	276.885	2.169	2.180–2.190 [14,15]
Exp.(a)	9.683	6.481	9.675	594.394		

(a) is reference [12]

The calculated a and c lattice parameters agree with the available experimental data to within 5.61% for $P12_1/c$ structure and 9.74% for $P2_1/c$ structure. In comparison, our b lattice parameter is smaller than the experimental value. This is due to the interatomic potentials used. We note that the geometric symmetry of the structures was preserved during optimisation. More importantly, we examined the bond length between the Ti and Cl atoms for each structure to further validate the structures. The equilibrium Ti-Cl bond lengths are comparable to the available experimental values to within 1%. The calculated Ti-Cl bond lengths in TiCl$_4$ are shorter, suggesting a strong interaction between the Ti and Cl atoms. Additionally, the Ti atoms in the TiCl$_4$ structures do not form a bond; thus, the Ti-Ti bond length was not observed.

3.2 Diffusion coefficient

We mapped the diffusion coefficients (DC) of Ti and Cl ions in the TiCl$_4$ medium to better understand their trajectories. This thermodynamic property is advantageous because we can trace their motions. Note that TiCl$_4$ is dissociated in the model leading to the formation of Ti and Cl ions. Figure 2 shows the comparison of the diffusion rate of Ti and Cl in $P12_1/c$ and $P2_1/c$ structures. The results clearly show higher diffusion for $P12_1/c$ (0.193 nm^2/s) compared to the $P2_1/c$ structure (0.021 nm^2/s) at 300 K, reflecting differences in structural constraints.

In figure 2a, the graph shows a linear increase in the diffusion of Ti and Cl ions, suggesting that the mechanism of diffusion is sensitive primarily to thermal agitation. This is consistent with fundamental thermodynamic principles. We observed that the ions diffuse similarly, suggesting that the diffusion process occurs at the same rate. At 1000 K and 1200 K, we note a “knee” behaviour which might be attributed to the self-diffusion of Ti and Cl. This behaviour has been observed previously in the diffusion of titanium, in which the self-diffusion of Ti was reported [16].

In figure 2b, the Ti and Cl curves exponentially increase at 50 – 2000 K. At 50 – 700 K, the curves coincide, and diffusivity is minimal for both Ti and Cl. This implies negligible movement. Diffusivity slightly increases at 800 K, then reverts to zero at 900 K. This anomalous behaviour might be due to temporal heterogeneity as demonstrated in a study by Akimoto and Yamamoto [17]. The diffusion rate increases at 900 – 2000 K, with Cl diffusing faster than Ti above 1100 K. This is due to its smaller size and lower charge than Ti.

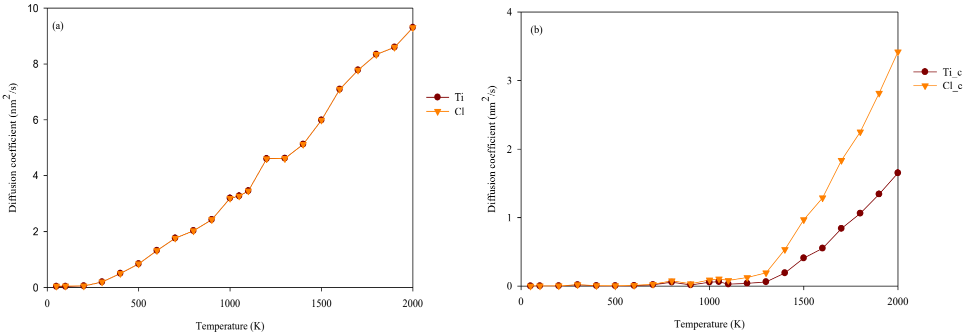

Fig. 2. Diffusion coefficient of the $TiCl_4$ medium at temperatures ranging from 50 K to 2000 K in (a) $P12_1/c$ and (b) $P2_1/c$ crystal modifications.

Figures 2a and 2b show that $DC_{P121/c} > DC_{P21/c}$, suggesting the $P12_1/c$ structure is more favourable and could be considered as a promising medium for producing high-purity titanium. The changes ("knee") in the diffusion curves around 1000 K and 1300 K correspond to the melting temperatures of the structures. Similar observations were noted for sodium chloride (NaCl) [18]. Additionally, the structures are both monoclinic, and we can attribute the difference in diffusivity to molecular interactions and structural organisation.

3.3 Effect of temperature variations on the total internal energy

The total internal energy is critical for understanding the energy dynamics in $TiCl_4$ mediums to optimise the titanium production process. Analysing this energy will help to determine the stability and efficiency of materials. Figure 3 compares the total internal energy for the $P12_1/c$ and $P2_1/c$ structures at varying temperatures. Both structures have a negative total internal energy, indicating that they are energetically stable and favourable within the temperature range of 50 – 2000 K.

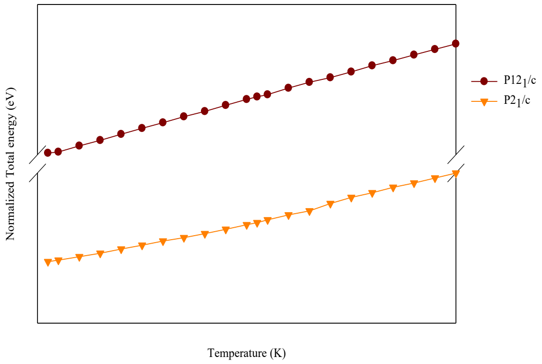

Fig. 3. Total internal energy of $TiCl_4$ mediums at 50 – 2000 K.

As expected, we note a linear increase in the energy with no observed phase transformation ("knee" behaviour) detected. This indicates that the structures remain preserved, reflecting the greater kinetic and potential energy contributions at higher thermal conditions. The $P2_1/c$ structure has more negative total internal energy values (-414250.00 eV), indicating that it has lower energy compared to the $P12_1/c$ structure (-369300.00 eV), resulting in an energy difference of -44950.00 eV. This suggests that the $P2_1/c$ structure is the most stable under the given conditions. These results quantify the thermodynamic state of the system and can support modelling of molecular behaviour.

4 Conclusion

The structures of $TiCl_4$ were validated using the GULP code, with the Ti-Cl bond lengths reproduced within 1% of experimental values, confirming the validity of the potentials. Diffusion coefficient results revealed that the diffusivity Ti and Cl increases with temperature, with the $P12_1/c$ structure showing higher diffusivity than the $P2_1/c$ structure. This indicates that the diffusion mechanism in $P12_1/c$ is primarily sensitive to thermal excitation. In $P12_1/c$, Ti and Cl ions diffuse at similar rates, suggesting coordinated behaviour as temperature increases, while in $P2_1/c$, Cl diffusivity becomes dominant above 1100 K due to its smaller size and lower charge. These findings highlight how structural differences influence ionic mobility in $TiCl_4$. The linear diffusivity trend in $P12_1/c$ indicates that diffusion depends on straightforward, predictable changes such as temperature. In the case of the $P2_1/c$ structure, the exponential diffusivity trend suggests that molecular interactions lead to varying energy barriers for diffusion. This can be observed in ionic transport within crystalline structures, resulting in activated diffusion characterised by the Arrhenius equation [19]. The total internal energy indicated that both structures are stable across the 50 – 2000 K temperature range, with the $P2_1/c$ structure showing more negative values and thus greater stability under the simulated conditions. These findings provide new quantitative data on the $TiCl_4$ transport properties, which were previously lacking, and offer a benchmark for future computational studies of $TiCl_4$ behaviour. Moreover, these results provide insights into the diffusion and thermodynamic behaviour of $TiCl_4$, which are relevant for understanding its role in titanium production processes. However, the simulations assume ideal conditions and may be tested with experiments. The broad temperature range (50–2000 K) introduces potential limitations: at very low temperatures (near 50 K), quantum effects may be significant, and at high temperatures (2000 K), maintaining phase stability and chemical reactivity can be challenging [20,21]. Acknowledging these limitations, our results provide valuable insights into $TiCl_4$ behaviour, supporting future efforts to refine models and improve the understanding of titanium production processes.

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Data is available on request from the authors

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