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Interatomic potential parameters for Li-Cl-Ti interaction

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Abstract. Alkali metals and alkali earth metals can be used as reducing agents of titanium halide in titanium production. Despite South Africa's position as being the major raw titanium material producer, titanium production is low and expensive as a direct consequence of the outmoded technology that is used in its extraction from raw materials such as the Kroll process. In this study, computational modelling techniques were employed to simulate the conditions for LiCl that will be suitable for generating a large quantity of metallic titanium in pure and powder form. We used a combination of density functional theory and molecular dynamics, employing FHI-aims, DL_POLY and GULP to characterize LiCl in a solid and molten form. The derived potentials reproduced the LiCl structure to within 1% in agreement with experimental data. More importantly, the melting temperature was deduced from the diffusion coefficient as 800 K which is closer to the experimental melting point of 878 K. Furthermore, the interaction of Ti-Li, Ti-Cl and Li-Cl-Ti were tested and gave reasonable results to set an environment for titanium clusters. The new pair potentials were deduced as Ti-Cl: $D_e=0.400$ $a_0=1.279$ $r_0=2.680$ and Ti-Li: $D_e=0.730$ $a_0=1.717$ $r_0=2.000$. The findings of this work will contribute towards the development of alternative ways of titanium production in a continuous and less expensive processes.

1. Introduction

Titanium has many applications in various industries such as in catalysis, medical and aerospace, where the fabrication of components with excellent corrosion and high temperature performance are significant [1]. Titanium clusters have shown great potential since they exhibit different properties compared to that of bulk structure. This has prompted a great interest in this field and thus extensive studies on Ti clusters are being performed [2, 3]. It has been reported that studies of titanium clusters are important to understand the evolution and growth regarding geometry and electronic properties [3]. In previous work, investigations by Zhao et al. [4], showed that the Ti clusters follow a pentagonal growth behavior that favors close-packed structures. Sun et al. [5] reported on the tetrahedral-, octahedral-, and icosahedral sequences being some of the size-dependent growth patterns. These structures or geometries can be obtained by either adding or removing atoms from certain basic motif or positions [5]. This is the underlying fundamental studies that may inform the process of titanium production.

Titanium powder can be produced commercially through thermochemical processes by reducing a precursor with a reductant which is either sodium (Na) or magnesium (Mg) [1]. However, the



reduction reaction occurs extremely fast and produces crystalline particles that tend to aggregate [6]. In other work, Seon and Nataf formed titanium powder by lithiothermic reduction of titanium tetrachloride (TiCl_4) in a molten salt reactor using a high-energy mixer that served to disperse undissolved lithium and gaseous TiCl_4 into the molten salt. This procedure may also break up any lumps of titanium that might form [7].

In this paper, we explore alternative means to gain understanding and knowledge on the titanium formation processes. We report the fundamental investigation using an alternative lithium chloride (LiCl) salt which has a similar structure as TiCl . We have performed molecular dynamics calculations on the LiCl structure using a combination of interatomic potentials from the CATLOW-library of potentials [8]. We also discuss the derivation of potentials for Ti in the LiCl system. A good reproducibility of Li-Cl, Ti-Cl, Cl-Cl interactions was achieved. These potentials are transferable to TiCl since all interactions have been considered.

2. Computational methodology

The initial configuration of LiCl was created from GULP [9] using a combination of potentials from the CATLOW-library that were firstly developed and validated. Molecular dynamics simulations were performed using DL_POLY code. A radial cut-off of 6.0 was used in a simulation of 216 atoms of LiCl system. The timestep was set at 0.001ps and the thermal data computed every 120 000 steps. The NVT ensemble using the Nosé-Hoover thermostat and barostat was run for 50000 steps to bring the system to equilibrium. Furthermore, pair potentials were deduced using the density functional theory FHI-aims [10, 11] code for the Ti-Cl and Ti-Li interactions. This was achieved by simulating a lithium ion, a chlorine ion and then a Li-Cl cube between two stable and symmetrical titanium clusters (Ti_7). The distance between the clusters and the Li^+/Cl^- was varied and the binding energies were calculated using the equation:

$$E_b = \frac{E_{FHI} - 2E_{Ti} - E_{alk}}{2},$$

where E_b is the binding energy, E_{FHI} is the energy from FHI-aims, E_{Ti} and E_{alk} are respectively, the energies of Ti and Li/Cl. The Morse-potential was used to investigate the interactions i.e. fit potentials.

3. Results and discussion

3.1. LiCl structure

The configured structure was firstly validated by comparing the lattice parameters of the LiCl structure with the experimental data. We observed that the interatomic Buckingham potentials used reproduced the structure to within 1% in agreement with experimental data. A lattice parameter of $a = 5.049 \text{ \AA}$ was obtained and it compared well with the experimental value as 5.070 \AA [8].

Elastic constants

The large dispersion about the behavior of C_{11} and C_{12} with respect to experiment, is mainly related to the correlation between the two quantities, both computationally and experimentally [8]. For C_{44} , the situation is different in that the dependence of C_{44} on the lattice parameter is very small, much smaller than for C_{11} and C_{12} [8]. In Table 1, the value of $C_{12} = C_{44}$ suggests that the Cauchy relation holds and that the material can be well described by pair-potentials. The calculated and experimental results agree as shown in Table 1.

Table 1. Calculated (Calc.) and experimental (Exp.) LiCl elastic constants C_{11} , C_{12} , C_{44} in GPa. Experimental data is from Ref. [12, 13].

System	C_{11}		C_{12}		C_{44}	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
LiCl	69.140	63.200	26.152	23.800	26.152	27.6

3.2. Thermodynamic properties

The mean square displacement and the diffusion coefficient were determined to understand the motion of Li^+ and Cl^- ions in the simulated system and the trajectories of these ions also traced.

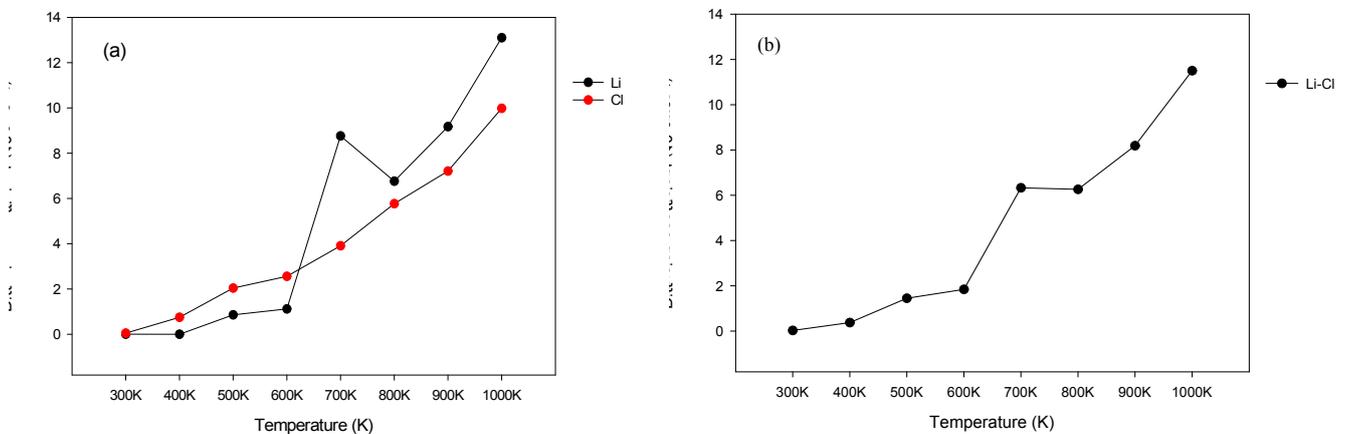


Figure 1. Diffusion coefficient ions (a) comparison between Li^+ and Cl^- , and (b) average for Li-Cl ions.

From the Figure 1(a-b), the diffusion coefficient depends exponentially on the temperature. The melting point was found to be 800 K which is closer to the experimental value of 878 K (605 °C -614 °C) [13]. This difference might be due to a slight mismatch in the potential parameters which have an important effect on the melting point, in this case an insignificant difference in the structural parameters was observed.

Radial distribution function.

In anion-cation radial distribution functions, the maxima and minima occur where there are corresponding minima and maxima hence the observation of a well-defined main peak at $\sim 3.13 \text{ \AA}$ for all the graphs depicted [13].

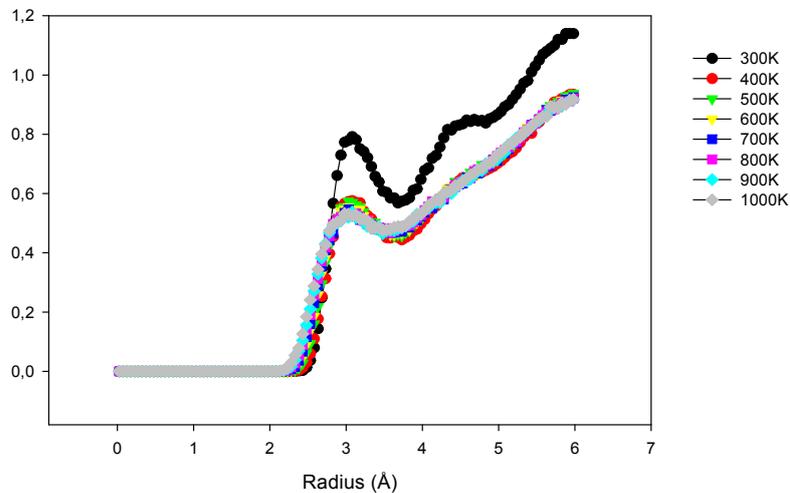


Figure 2. Radial distribution function for LiCl.

Figure 2 shows the radial distribution function of LiCl corresponding to different temperatures. The peak at 300 K shows that the structure is still intact, which is what we expect to observe at lower temperatures. Also, the height of the first peak of the radial distribution curve decreases with temperature increment while the width of the peak increases to almost a straight line. This might indicate that at higher temperatures the interaction between Li-Cl is weaker due to the increase in the kinetic energy of the atoms suggesting melting. Furthermore, the broader second peak at 300 K shows that there are still observable interactions of the atoms in the system, but this peak starts disappearing around 800 K, implying that the structure is beginning to lose its morphology as atoms begin to be randomly distributed.

3.3. Fitting pair potentials for the interaction of Ti in LiCl systems

The comparison between the DFT results generated using FHI-aims and Morse-potential results.

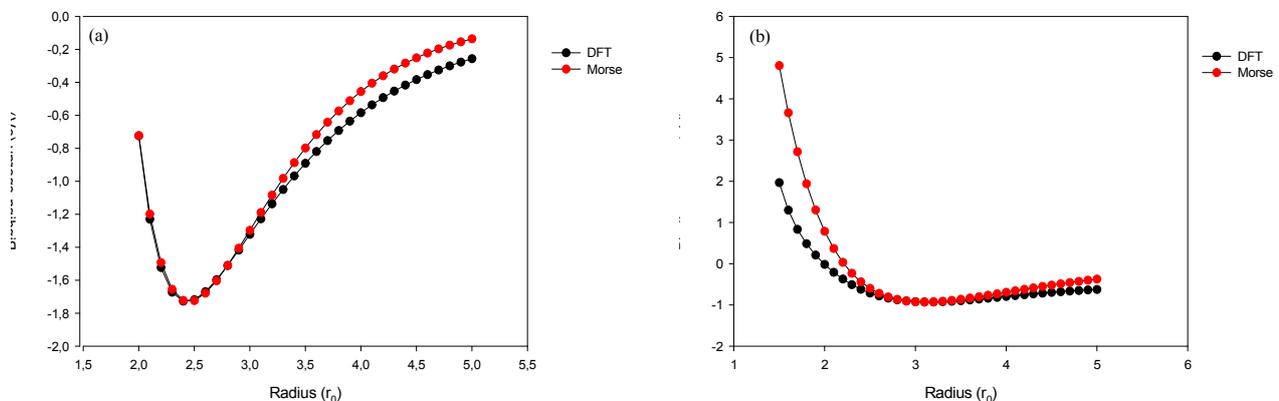


Figure 3. The interaction between (a) Ti-Cl and (b) Ti-Li for the DFT and Morse potential.

Figure 3(a-b), shows the interaction of the Ti-Li and Ti-Cl deduced from binding energies calculated from FHI-aims energies. The DFT results show similar trends with the Morse-potential curves and this observation provides guidance on which potential parameters will be best suited to describe the interactions of the system.

Table 2. Morse pair potentials.

	Ti-Cl		Ti-Li	
	Initial	Final	Initial	Final
D_e	0.400	0.400	0.033	0.730
a_0	1.279	1.279	0.857	1.717
r_0	2.681	2.681	3.875	2.000

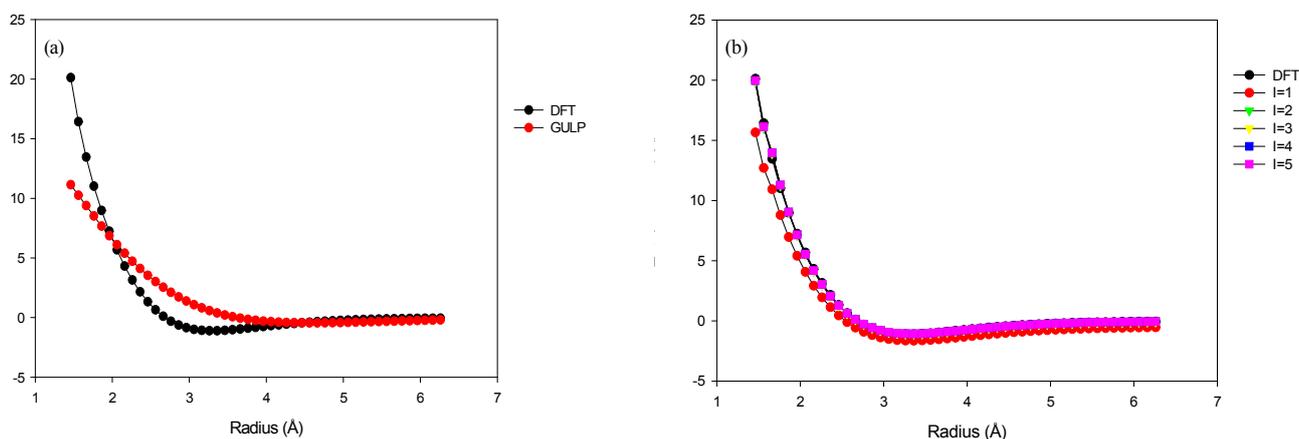


Figure 4. Energy Vs Radius curve for the Li-Cl-Ti system. (a) Comparison of DFT and GULP fitting, (b) fitting of Morse potentials from adjusting the D_e and r_0 parameters and comparing with DFT.

In Figure 4(a), the fitted Ti-Cl and Ti-Li parameters were noted when the final sum of squares was close to zero. However, it was observed that the GULP curve shows that the parameters used for fitting are not the best ones since there is no alignment between the DFT and GULP curves from Figure 4(a). The Ti-Cl parameters were unchanged, while those of Ti-Li were changed since these were far from the final sum of squares of close to zero. Thus, an adjustment in the D_e and r_0 parameters to better align the graphs was done. Hence, Figure 4(b) shows the fitting of Morse pair potentials and the parameters are given in Table 2.

4. Conclusion

The derived potentials reproduced the LiCl structure to within 1% in agreement with the experimental data. The elastic constants are also in agreement with experimental observation whilst still obeying the Cauchy relation. It was predicted that the melting temperature was 800 K which is closer to 877 K [13]. More importantly, from Figure 4 we observed the DFT and Morse curve alignment. This suggests that the derived potentials could be used to set an ideal environment for exploring the growth and evolution of the titanium clusters in a LiCl solution.

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