

COMPUTATIONAL SIMULATION OF MOLTEN TITANIUM-ALUMINIUM METAL AND ALLOYS

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ABSTRACT

Mintek has produced 35-40% Ti-Al alloys in DC Arc Furnace campaigns, however, process difficulties encountered appear related to poor understanding of the alloys' physical properties. Making measurements at around 1500°C is often impractical or expensive - Atomistic Computational Modelling (Embedded Atom Method, EAM) is ideal for studying alloys, leading to process improvements (efficiency/reducing environmental impact). Physical properties predicted include density, enthalpy, thermal expansion and heat capacity. EAM showed Ti-rich alloys to be the densest, most stable and highest melting – agreeing with experimental findings of furnace campaigns. Furthermore, modelling suggests 18-59% Ti-Al alloys have stronger amorphous propensities than other Ti-Al alloys.

INTRODUCTION

Mintek specialise in mineral technology and the pyrometallurgy division employs pilot-scale DC arc furnaces up to 5.6MVA in smelting process research and development. Titanium-aluminium alloys are an area of interest [1] with useful properties especially for refinement of alloys grains in the aluminium casting industry. Two campaigns have been performed at Mintek in July/September 2006 to produce Ti-Al alloys containing around 35-40% Ti. The process involves aluminothermic reduction of titanium dioxide (pure TiO₂, rutile, etc) to produce a combination of products including metals/alloys such as Ti, Ti₃Al, TiAl, TiAl₃ and Al. These two campaigns were partially successful owing to a large amount of slag produced along with a buildup of unknown high melting compounds found during the furnace digout. Any improvement in the process in terms of improved efficiency, reduction in slag or environmental impact would be invaluable. Computational modelling or simulation can yield vital information and a better understanding of the process, leading to such improvements. Furthermore, most experimental measurements at furnace operating temperatures around 1600°C are highly impractical and/or expensive, so computational atomistic methods are an ideal choice for determining physical properties and behaviour.

The Embedded Atom Method (EAM) was developed by Daw and Baskes [2,3] and extended for modelling particular metals [4] and alloys [5] by Oh and Johnson. The EAM is well suited for modelling metals, treating the system in the way metal atoms are usually conceptualised: the metal atoms in a “sea” of electrons. The energy of a box of simulated atoms is computed as the sum of pair potential and embedding function contributions. Pair potentials are commonly used to describe systems at an atomic level and are effectively non-bonded interactions similar to the well known van der Waals interactions or London forces [6]. The embedding function describes the embedding of a metal atom in the “sea” of electrons due to the electron density σ of the surrounding atoms. Equations 1-3 describe in more details how interaction energies are defined:

$$E_{\text{total}} = \sum E_i \quad (1)$$

$$E_i = F_i(\sigma_i) + \sum \Phi_{ij}(r_{ij}) \quad (2)$$

$$\sigma_i = \sum f_j(r_{ij}) \quad (3)$$

The total energy E_{total} is the sum of the contributions E_i of each atom i . Each E_i comprises embedding ($F(\sigma_i)$) and pair potential ($\Phi(r_{ij})$) contributions. $F_i(\sigma_i)$ is the energy to embed atom i in the electron density resulting from all the other atoms at the point i . All other atoms j contribute to this electron density σ_i according to their distance r_{ij} from atom i and a spherically symmetric density function $f(r_{ij})$. The pair potential term $\Phi_{ij}(r_{ij})$ is the sum of all i - j atom pairs interacting in a non-bonded manner. For alloys comprising metals of type A and B, there are three choices for the pair potentials, namely $\Phi^{\text{AA}}(r_{ij})$, $\Phi^{\text{BB}}(r_{ij})$ and the mixed pair $\Phi^{\text{AB}}(r_{ij})$, compared to the pure metal cases of only $\Phi^{\text{AA}}(r_{ij})$ or $\Phi^{\text{BB}}(r_{ij})$. No mixed term is required for the embedding function or electron densities in the case of alloys since the pure metal functions can be used. In a molecular dynamics (MD) simulation, the box of atoms is simulated to move in a natural way according to Newton's Laws [7,8]. Since subsequent positions of atoms can be predicted, a trajectory (a “movie” of “snapshots”) is generated. The trajectory can be analysed to yield a huge amount of information including structural, dynamic and thermodynamic properties.

Ti-Al systems have been studied in the solid state [9-12] and in the liquid/molten state by Shimono and Onodera [13, 14], and Han et al [15]. Pure metals modelled in the liquid state include Al [16], Cu [17,18], while Slorovitz et al [19] has examined Ag, Au, Cu, Ni, Pd, and Pt. Liquid alloys such as Ni₃Al [20] and Ni-Cu [21,22] have also been studied. Shimono and Onodera [13,14] have explored liquid to amorphous transition for Ti-Al alloys, while Han, Chen and Guo [15] have predicted the behaviour in terms of temperature of density, enthalpy and heat capacity without exploring phase transitions.

METHODOLOGY

We have performed MD simulations using DL_POLY_2.18 [23] for a number of Ti-Al alloys and pure metals using the EAM formalism. The isobaric ensemble (NPT) was employed and a LoadLeveler script was developed to allow Simulated Annealing calculations to be performed. This entailed performing an equilibration simulation at 2100K of 200ps, followed by 50ps equilibration simulations at 2090K, 2080K, ... 2010K (i.e., reducing the temperature by 10K for each new simulation). Longer data collection simulations were implemented at multiples of 100K (2000K, 1900K, ... 100K) and each of these comprised 100ps equilibration and 200ps data collection. Simulated annealing was performed in this manner from 2100K down to 100K. Simulation predictions were checked to ensure stable MD behaviour in terms of temperature, volume and appropriate energies. Extremely fast simulation of cooling/heating of the order of 10^{11} K s⁻¹ is a consequence of timescales used in MD, so melting may be predicted at significantly lower temperatures or solidification may not be seen in some circumstances.

Two different EAM models were employed for the Ti-Al simulations. Models for pure Ti and Al have been developed by Oh and Johnson [4] and the required Ti-Al alloy pair potentials have been generated by Shimono and Onodera [13] using an established procedure [5]. The first model will be referred to hereafter as the “Shimono” model and was developed using solely physical measurement data. The second model developed by Zope and Mishin [12,24] is based on both physical and quantum mechanically generated data and is subsequently referred to as the “Mishin” model. The work of Han et al [15], used for comparison purposes in this paper, was conducted using the Mishin model.

RESULTS AND DISCUSSION

Density and enthalpy curves produced from the simulations are shown in Figures 1-4 below for the pure metals Ti and Al, as well as their alloys Ti₃Al, TiAl and TiAl₃. The curves presented have all been generated using the Mishin model, which is subsequently shown to be a better model than that of Shimono.

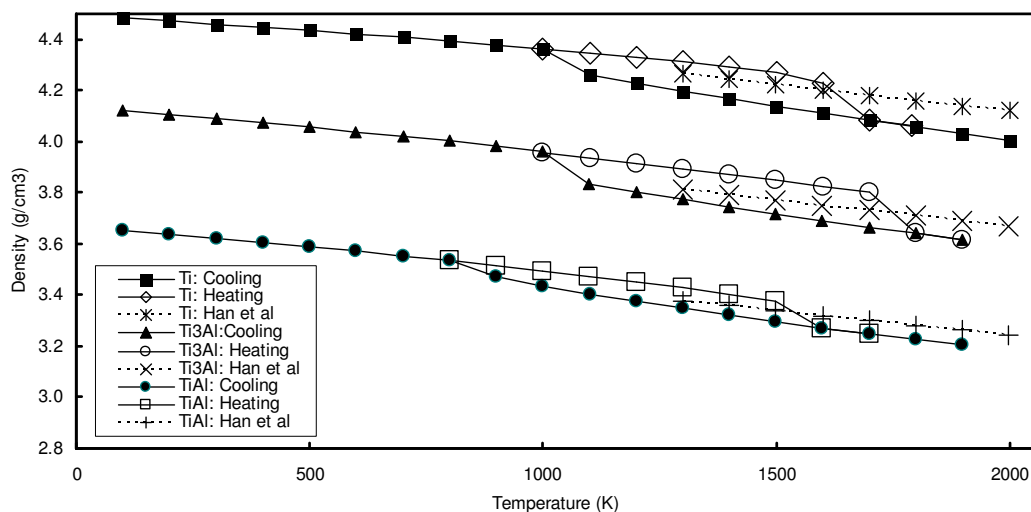


Figure 1 – Density behaviour with temperature for Ti, Ti₃Al and TiAl

The behaviour of density with temperature for Ti, Ti₃Al and TiAl is shown in Figure 1. Heating and cooling curves reveal heating and cooling cycles with both a glass transition and a melting point (at lower and higher temperatures, respectively). The curves derived by Han et al [15] are also shown for comparison purposes and are consistent with the current predictions in terms of values and slopes - this is to be expected since Han et al [15] have also used the Mishin [12] model. The slopes of density-

temperature curves are proportional to the linear thermal expansion coefficient α (shown later in Table 1). The predicted melting point for Ti in the range 1600-1700K significantly underestimates the experimental value of 1941K, which is probably attributable to extremely rapid heating rates characteristic of MD simulation. No experimental melting points for the Ti_3Al and TiAl alloys were available.

The density-temperature behaviour of TiAl_3 and Al is illustrated in Figure 2. TiAl_3 does not yield any heating-cooling cycles – instead there is a phase transition occurring with a change in slope but without the expected jump in density. This is indicative of a second order phase transition (one which occurs with only a change in slope and without any latent heat) which could correspond to an amorphous transition. Consistency is seen between our predictions and the literature predictions of Han et al [15] as is to be expected. The cooling curve for Al did not show any crystallisation – probably attributable to rapid cooling characteristic of MD simulation. Hence, results of simulations performed using crystal starting configurations are also shown. The predicted melting point for Al of 850-855K is reasonable compared to the experimental value of 933.47K.

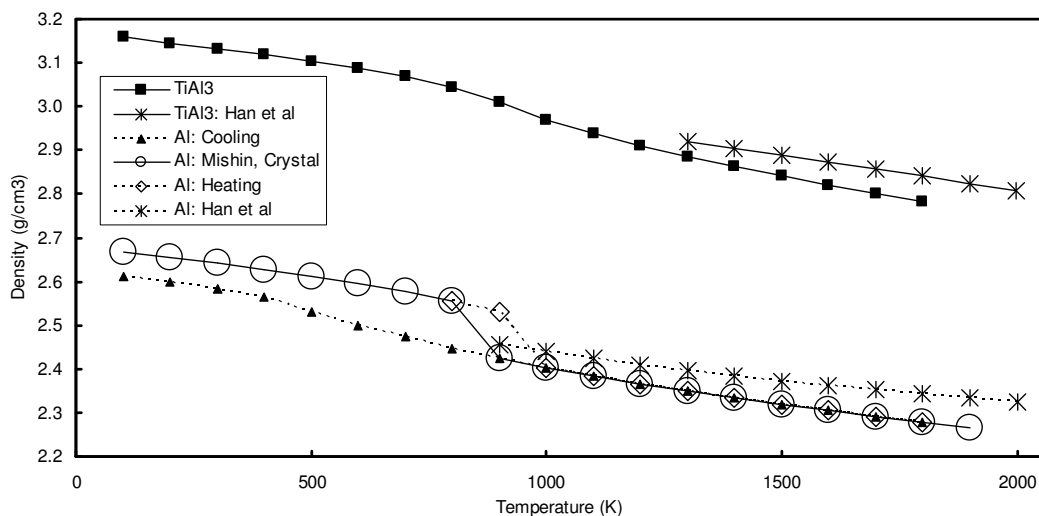


Figure 2 – Density behaviour with temperature for TiAl_3 and Al

The enthalpy-temperature behaviour for Ti and Ti_3Al is illustrated in Figure 3, while the corresponding behaviour for TiAl , TiAl_3 and Al are shown in Figure 4. The behaviour seen for density-temperature curves is mirrored in these curves in terms of heating-cooling cycles, melting point, glass transition temperature and second order phase transitions. Agreement with Han et al [15] is again found as is to be expected. The slope of an enthalpy curve yield the heat capacity at constant pressure C_p .

In order to illustrate the differences between simulated solid and liquid structures, the Radial Distribution Function (RDF), $g(r)$, for Al above and below the melting point (at 900K and 1000K) are shown in Figure 5. A higher more defined first peak is seen for the solid than for the liquid; a shoulder is evident at around 4.2\AA in the solid; while the liquid shows a rather flat second peak. These facts indicate the solid is more structured as is expected.

Since a second order phase transition was observed for TiAl_3 , further systems were studied (using much longer equilibration times) to determine whether this phenomenon is unique to TiAl_3 or not. It is clear from Figure 6 that some of the other systems behave similarly, such as Ti_4Al_5 , Ti_2Al_3 , TiAl_6 and TiAl_8 . Hence, most 18-59% Ti-Al alloys appear to show this behaviour and thus have a stronger amorphous propensity than other Ti-Al alloys.

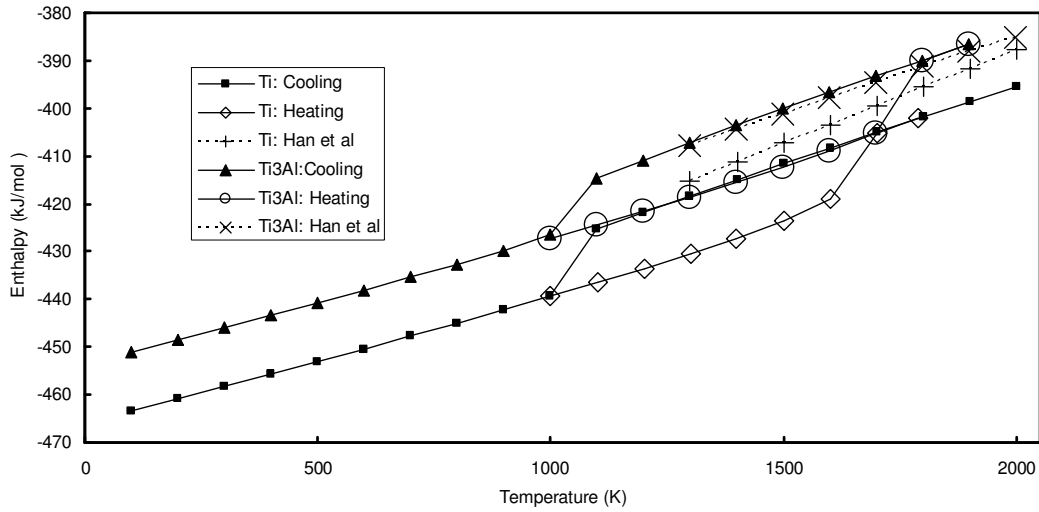


Figure 3 – Enthalpy behaviour with temperature for Ti and Ti₃Al

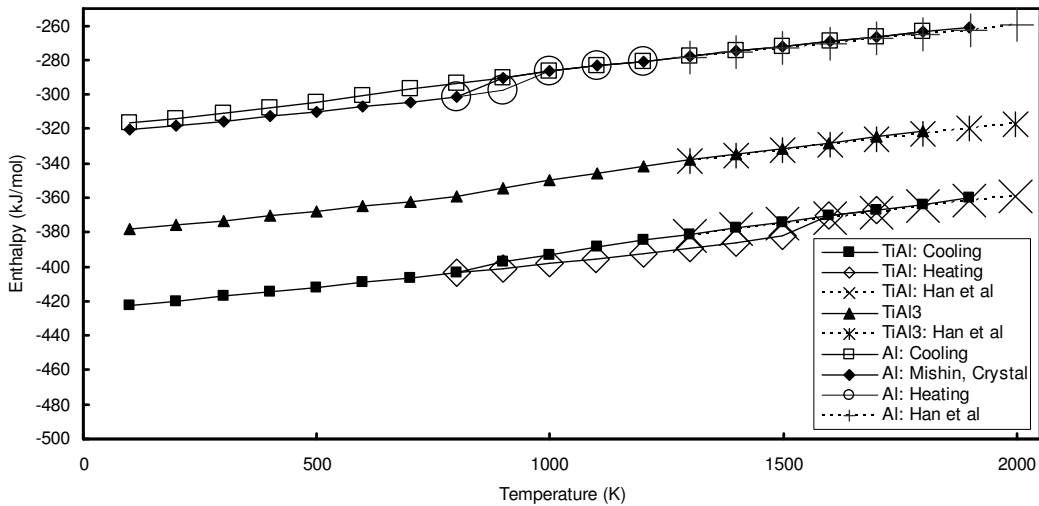


Figure 4 – Enthalpy behaviour with temperature for TiAl, TiAl₃ and Al

The physical properties of density (ρ), linear thermal expansion coefficient (α) and heat capacity (C_p) have been determined from curve fitting of the density and enthalpy predictions of the Mishin (Figures 1-4) and Shimono models. Linear and quadratic curves have been fitted and the appropriate one selected in each case. The values or slopes at 298K obtained from these fits yield the above physical properties which are listed in Table 1 and compared to available experimental literature values. For Al, the Shimono model predicts a slightly better ρ value than that of Mishin, while C_p and α are significantly better predicted using Mishin than Shimono. For Ti, all three properties are better predicted by the Mishin model. Although no experimental values are available for TiAl₃, the values of all three quantities appear reasonable. The Mishin model predicts TiAl and Ti₃Al densities better than the Shimono model does. Overall, the Mishin outperforms the Shimono model and is the better choice for the Ti-Al systems. This conclusion is in line

with the postulate that using quantum mechanical (QM) data in parameterisation results in a better model since the Mishin model was developed using QM and experimental data, while the Shimono model is solely based on experimental data.

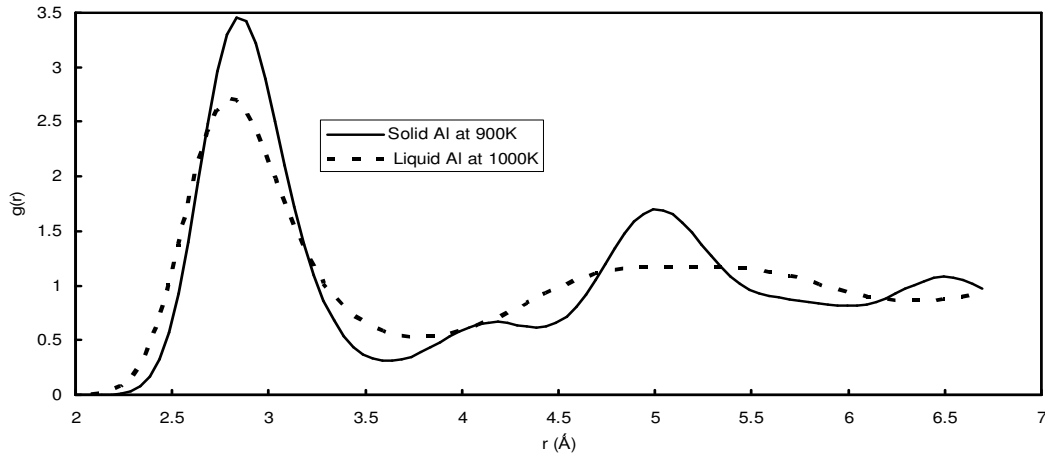


Figure 5 - Radial Distribution Function $g(r)$ for Al solid and liquid from heating simulation

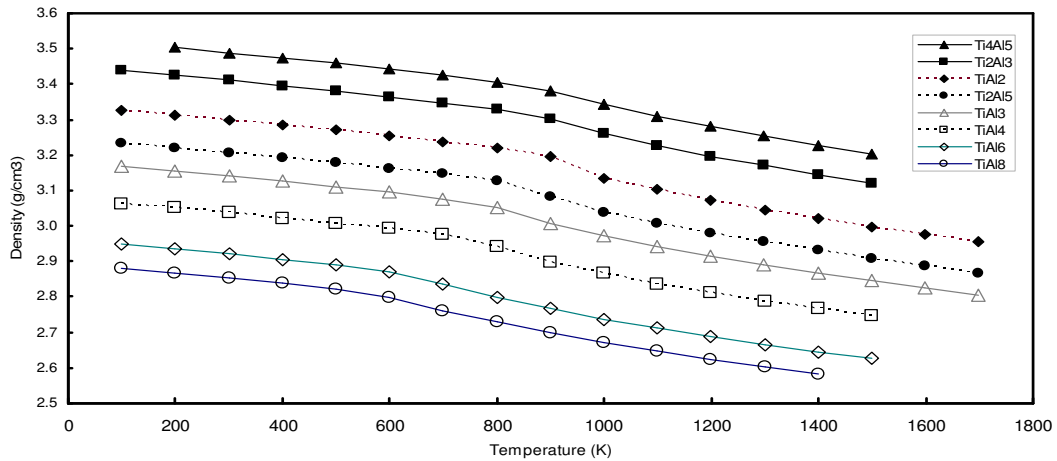


Figure 6 – Predictions of possible second order phase transitions using the Mishin model

In order to understand the behaviour of metals and alloys in the DC arc furnace at temperatures around 1600K and 1800K, the properties of melting point (MP), glass transition temperature (GT), density and enthalpy predicted using the Mishin model are tabulated below (Table 2). Clear trends are evident when one examines increasing Ti content, with an increase in MP, GT and density. Further, enthalpy decreases with increasing Ti content, indicating increased stability. Hence, Ti-rich compounds are the most stable and have higher MP and densities. Such compounds are likely to form and sink to the bottom of the furnace – in line with the buildup of high melting compounds observed in the DC arc furnace.

Table 1 - Physical properties of metals and alloys predicted using the Mishin and Shimono models

Metal/Alloy	Model/Experiment	Density (g cm ⁻³)	C _p (J mol ⁻¹)	α (10 ⁻⁶ K ⁻¹)
Al	Mishin	2.58	27.8	17.9
	Shimono	2.62	26.4	30.2
	Literature	2.6989 [25]	24.3 [25]	22.8 [25]
TiAl ₃	Mishin	3.13	25.8	15.0
	Shimono	2.97	26.0	23.1
TiAl	Mishin	3.62	25.8	15.8
	Shimono	3.36	26.0	19.2
	Literature	3.7-3.9 [25]	-	-
Ti ₃ Al	Mishin	4.08	25.6	14.3
	Shimono	3.82	25.4	18.6
	Literature	4.1-4.7 [25]	-	-
Ti	Mishin	4.46	25.4	9.6
	Shimono	4.28	25.7	17.8
	Literature	4.507 [25]	25.00 [25]	8.41 [25]

Table 2 –Metal/Alloy Predicted Properties using the Mishin Model at Furnace Operating Temperatures

	Al	TiAl ₃	TiAl	Ti ₃ Al	Ti
MP (K)	800-900	-	1500-1600	1700-1800	1600-1700
GT (K)	-	800-900	800-900	1000-1100	1000-1100
Density at 1600K (g cm ⁻³)	2.31	2.82	3.27	3.82	4.20
Enthalpy at 1600K (kJ mol ⁻¹)	-269	-328	-370	-409	-419
Density at 1800K (g cm ⁻³)	2.28	2.78	3.23	3.64	4.06
Enthalpy at 1800K (kJ mol ⁻¹)	-264	-322	-364	-390	-402

CONCLUSION

An understanding of the behaviour of Ti-Al pure metals and alloys in the DC arc furnace at Mintek has been gained through molecular dynamics simulations employing two different EAM models (Mishin and Shimono) and using a simulated annealing procedure. The physical properties of density and enthalpy have been predicted over a large temperature range for these metal systems, while the heat capacity and linear thermal expansion coefficient have been predicted at room temperature. Heating and cooling cycles were evident for most of the metals and alloys. Second order phase transitions were predicted for Ti₄Al₅, Ti₂Al₃, TiAl₃, TiAl₆ and TiAl₈ and this suggests that 18-59% Ti-Al alloys have a stronger amorphous propensity than other Ti-Al alloys.

The predictions of physical properties and behaviour are in reasonable agreement with theoretical and experimental literature. Predictions of density and enthalpy at furnace operating temperatures (1600 and 1800K) revealed that Ti-rich compounds are the most stable with relatively high melting points and densities, and are thus likely to sink to the bottom of the furnace. This is in line with the experimental findings in the DC arc furnace of a buildup of high melting compounds in the hearth.

The Mishin model was shown to be superior to that of Shimono. The former model is based on both quantum mechanical and experimental data, while the latter is derived from solely experimental data. Hence our results are in line with the postulate that quantum mechanical data should be included when formulating such models. Since our interest is in the molten/liquid state and these models were both based on solid state data, a more suitable model would employ sufficient liquid phase data. Hence, we intend developing models for Ti-Al systems and other metals which are tailored to the liquid phase by parameterising using quantum mechanical data and a force matching procedure [26,27].

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