Abstract

Results of first-principles, density-functional, TBLMTO –ASA calculations on the closely related ZrGa_2 and HfGa_2 structures of the reentrant phase TiAl_2 intermetallic compound is reported. Theoretical calculations shows, that HfGa_2 structure is more stable structure than ZrGa_2 in agreement with experimentalists. However, the other structure is very close in energy indicating the possibility of the presence of these two phases in equilibrium over a range of temperature. Also it reports a very good agreement between the calculated equilibrium lattice parameter, and the experimental results. The cohesive properties of this system are calculated and a possible comparison of the calculated quantities with available experimental data are presented here.

Introduction:

The Titanium trialuminide is a promising structural material because of its high melting point, lower density and superior oxidation resistance, but trialuminides are more brittle compare to other intermetallic compounds among the titanium based binary alloys. It is to be noted that TiAl is very close to the standard alloy Ti-48Al-2Nb-2Cr whereas, TiAl_3 is a highly brittle material with high hardness [1]. TiAl_2 lies inbetween TiAl and TiAl_3 with improved desirable properties of both. Thus, TiAl_2 is used for oxidation resistance coatings on TiAl_3 and TiAl structural compounds. Mabuchi et al [2] used the pack cementation technique to produce TiAl_3 coatings on TiAl, and found that the intermediate layers crystallise in HfGa_2 structure type with the concentration at.77% of Al and at.33% of Ti. The TiAl_2 phase was first identified by Potzschke and schubert in 1952 [3]. They determined that, TiAl_2 has the HfGa_2 type crystal structure, a tetragonal structure containing 24 atoms in its unit cell. Some recent experimental works, on the structural and phase stability of the intermetallic compounds, in the Ti-Al system, containing between 24 and 42 at% of Ti have been performed by Loiseau and Vannuffel [4] Kaltenbach et al and Suhuster and Lpser [5]. The results for the TiAl_2 phase field from these three studies are some what contradictory. According to Kaltenbach et al the single phase TiAl_2 is stable upto 1117º C after that it decomposes into γ-TiAl and ξ(Al_{11}Ti_5) and on further heating, about 1415º C it liquefies. According to Loiseau and Vannuffel work, TiAl_2 is a reentrant phase, that is it has the same structure at low and high temperatures, but a different structure at intermediate temperature. In the
intermediate temperature the crystal structure is of HfGa$_2$ type. At low and high temperature TiAl$_2$ has formed in the orthorhombic ZrGa$_2$ type structure, which is closely related to HfGa$_2$ structure. A detailed research, on the Ti-Al phase diagrams between the compositions TiAl$_3$ and TiAl, by Schuster and Ipser revealed two polymorphs of TiAl$_2$. But there was no evidence for the reentrant phase of TiAl$_2$. As this finding is in contradiction to that of Mabuchi et al, an attempt is made to theoretically investigate the problem which may throw more light into the structure of TiAl$_2$.

Self-consistent band structure calculation of TiAl$_2$ have been performed using the standard Tight Binding Linear Muffin-Tin Orbital Method within the atomic sphere approximation (TBLMTO –ASA)[6-8]. Combined correction terms have been included in order to obtain more accurate results. These calculations are based on the density functional theory of Hohenberg, Kohn and Sham with the local density approximation. The von Barth-Hedin local density form has been used for the exchange and correlation potential. The valence states (3d$^2$,4s$^2$ for Ti and 3s$^2$,3p for Al) have been iterated in the self-consistency cycles, where as the frozen core approximation has been assumed for the remaining lower state. The calculation have been performed with a mesh of 370 k points for HfGa$_2$ and 199 k points for ZrGa$_2$ in the irreducible wedge of the Brillouin Zone (IBZ). The variation of the total energy from iteration is less than $10^{-5}$ Ryd.

The tetragonal HfGa$_2$ crystal structure (space group I4$_1$/amd)[9] contains 24 atoms per unit cell; i.e 16 Al atoms and 8 Ti atoms (Fig.1). With the atomic positions Al (0 0 0.25), Al (0 0 0.44) and Ti (0 0 0.074). The orthorhombic ZrGa$_2$ (space group Cmmm ) structure contain 12 atom per unit cell. Twelve atoms are of with the atomic positions Al (0 0 0), Al (0.5 0 0.5), Al (0.176 0.0 0.5), Ti (0.351 0 0 ) and the remaining are of equivalent positions.

The total energies calculated as a function of unit cell volume for the two phases is shown in fig.2. We have plotted the total energy with respect to a reference energy (10693 Ry.). From that results the equilibrium lattice constants, bulk module and heat of formation are obtained. For the tetragonal phase, we started the calculation with the experimental lattice constants $a = 3.967$ Å and $c = 24.125$ Å with $c/a = 6.081$. We
Table 1. Cohesive properties of TiAl₂ in HfGa₂ and ZrGa₂ structures.

<table>
<thead>
<tr>
<th></th>
<th>HfGa₂ – Structure type</th>
<th>ZrGa₂ – Structure type.</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Present</td>
<td>Exp.</td>
</tr>
<tr>
<td>Lattice parameter (Å)</td>
<td>a=3.957</td>
<td>3.967</td>
</tr>
<tr>
<td></td>
<td>c=24.0224</td>
<td>24.125</td>
</tr>
<tr>
<td></td>
<td>c/a=6.125</td>
<td>6.081</td>
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<td></td>
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<td></td>
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<tr>
<td>Cohesive energy Ecoh (eV/atom)</td>
<td>0.556</td>
<td>----</td>
</tr>
<tr>
<td>Heat of formation -ΔH (eV/atom)</td>
<td>0.263</td>
<td>----</td>
</tr>
<tr>
<td>N(E_F) (states/Ry./Cell)</td>
<td>50.313</td>
<td>---</td>
</tr>
<tr>
<td>E_F (Ry.)</td>
<td>-0.0336</td>
<td>---</td>
</tr>
<tr>
<td>Bulk modulus B₀ (Mbar)</td>
<td>1.3123</td>
<td>---</td>
</tr>
<tr>
<td>B₀’</td>
<td>3.618</td>
<td>---</td>
</tr>
<tr>
<td>Electronic specific heat coefficient γ (mJ mol⁻¹ K⁻²)</td>
<td>8.72</td>
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</tr>
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</table>

Then varied the c/a ratio at the theoretical volume to get the theoretical c/a ratio. We obtained the lattice constants a=3.957 Å and c=24.0224; and a bulk modulus 1.312 Mbar. In the orthorhombic structure, starting from the experimental cell volume, the equilibrium values of c/a and b/a were obtained by energy minimization procedure. The equilibrium values of c/a and b/a are 0.3308 and 0.3268 respectively.

As expected, lattice parameters are underestimated by 0.5 – 1% compared to the experimental values due to the neglect of zero-point motion and the overestimation of bonding by LDA, as discussed in detail by Maruzzi et al [10].

Total energy calculations enables one to decide the stability of the systems. In general, the system with lower total energy is said to be the stable one. The total energies were calculated for these two competing structures for various volumes. The variation of total energy with volume is shown in the Fig.2 which clearly shows the minimum total energy for HfGa₂, indicating its stability than the other.
The stability of the system can also be studied using the heat of formation and the number of electrons at the Fermi energy $N(E_F)$ in the density of states histogram. The cohesive energy and heat of formation are calculated for both the HfGa$_2$ and ZrGa$_2$ structure types following the usual procedure \cite{11-12}, and is shown in table 1. The heat of formation is higher (more negative) for HfGa$_2$ structure type than the other. There is a strong correlation observed between stability and position of Fermi level in the DOS curve in the binary alloy, that is, if the $E_F$ falls on the pseudogap which separates bonding states from the anti bonding/nonbonding states in a particular structure, the system will be more stable \cite{13}. In other words, the stable structure has always low $N(E_F)$. In Fig.3, the $E_F$ has fall near the pseudogap at $-0.0336$ Ry. for HfGa$_2$ structure, and $-0.0385$ Ry. for ZrGa$_2$ structure. The values of $N(E_F)$ is low for HfGa$_2$ which signifies the stability of HfGa$_2$ structure type than ZrGa$_2$.

Thus from the cohesive energy, heat of formation $N(E_F)$ and the total energy calculations we conclude that HfGa$_2$ structure is more stable than the other in agreement with the experimental report of Mabuchi et al.

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References