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## Stability of Ordered B2- $\beta_0$ and Disordered BCC- $\beta$ Phases in TiAl - A First Principles Study

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**Abstract.** Either at higher temperatures or when a certain alloying element content is exceeded,  $\gamma$ -TiAl alloys contain the  $\beta$  phase (bcc) or its ordered derivate  $\beta_0$  (B2). The relatively soft  $\beta$  phase can facilitate hot deformation, but  $\beta_0$  is detrimental for creep strength and ductility. Thus, knowledge about  $\beta_0 \rightarrow \beta$  phase transformation is desirable. Surprisingly, even for the binary Ti-Al system it is under discussion whether the ordered  $\beta_0$  phase exists. Also, the effect of alloying elements on the  $\beta$  phase ordering is still unclear.

In the present work the ordering of the  $\beta$  phase in binary Ti-(39,42,45)Al and ternary Ti-42Al-2X alloys (X=Fe, Cr, Nb, Ta, Mo) which was experimentally investigated by neutron and high energy X-ray diffraction is compared with the results of first principles calculations using density functional theory. Except for Cr the experimentally determined and the predicted behavior correspond.

### Introduction

$\gamma$ -TiAl alloys are promising lightweight structural materials for high temperature applications due to their low density, high specific strength and good corrosion resistance. Accordingly, they were recently introduced as a material for low pressure turbine blades in civil aero engines partly replacing the twice as heavy Ni-base superalloys [1,2]. The alloys have aluminum contents between 40 to 48 at.% and consist predominantly of the ordered intermetallic phases  $\gamma$ -TiAl (L1<sub>0</sub> structure) and  $\alpha_2$ -Ti<sub>3</sub>Al (D0<sub>19</sub> structure). The  $\gamma$ -phase has the highest volume fraction explaining the name  $\gamma$ -TiAl alloys for this type of materials [1,3]. Other metallic and intermetallic phases may be present depending on temperature and alloy composition [1,4,5]. The disordered  $\beta$ -Ti phase with bcc structure is a high temperature phase in the binary Ti-Al system, which can also be present in  $\gamma$ -TiAl alloys with sufficiently high contents of  $\beta$ -stabilizing alloying elements and lower Al-contents [1,4,6,7]. The  $\beta$ -phase is of interest as it can facilitate the processing of  $\gamma$ -TiAl alloys by e.g. forging if present at the desired forging temperature. Unfortunately, such alloys often also contain either  $\beta$ -phase or its ordered low temperature derivative  $\beta_0$  with B2 structure at lower temperatures. While the presence of  $\beta$ -phase at high temperatures is desired due to its positive effects on processing the presence of  $\beta$  or  $\beta_0$  at service temperatures is considered as detrimental for the mechanical properties. They can embrittle the material and reduce its creep resistance. Given this importance of the  $\beta$ - and  $\beta_0$ -phase with respect to processing and mechanical properties, it is surprising that reliable information especially about the ordering and disordering of those phases is scarce and contradictory. It is neither fully clear whether ordered  $\beta_0$ -phase with B2 structure exists in the binary Ti-Al system nor which alloying elements promote ordering of  $\beta$ - to  $\beta_0$ -phase, e.g. [6,7].

The authors used neutron diffraction to investigate the presence of the ordered  $\beta_0$ -phase in a number of binary and ternary  $\gamma$ -TiAl alloys [8]. It was found that the ordered  $\beta_0$ -phase does not exist at any temperature in the binary system. The same is true for alloys containing 2 at.% of the elements Ta or Nb while ordered  $\beta_0$ -phase was found if the same amount of Cr, Mo or Fe was alloyed.

The present work is meant as a theoretical supplement of this experimental work. Whether a phase exists in its ordered or disordered structure, assuming that chemical equilibrium is reached, only depends on the Gibbs free energies of both phases and the Gibbs free energies of other competing phases in the system. The Gibbs free energy is a combination of the energy of formation of the phase

and its entropy representing the temperature dependent part of the Gibbs free energy [9]. The so called CALPHAD method is able to predict Gibbs free energies of different phases but therefore relies on thermodynamic factors describing for example the interaction between different alloying elements which are contained in databases [10]. These databases are mainly based on experimental observations. Thus, in the situation present here where the experimental knowledge is rather contradictory comparing the investigations in [6,7,8] CALPHAD seems not to be suited to shed further light on the situation from a modelling point of view. Energies of formation are solely based on the interatomic bonding and thus in principle can be calculated ab-initio. Density functional theory (DFT) provides a framework to solve Schrödinger's equation providing energies of ground states which can be used to calculate energies of formation [11]. Unfortunately, it is difficult to calculate non stoichiometric systems where atomic species are not located on specific lattice sites by DFT but a number of methods have been developed to overcome this problem. Well established in the field of materials science is the use of so called special quasirandom structures (SQS) [12]. These are constructed in a way to mimic the atomic surrounding of a solid solution of the desired off-stoichiometric composition. This approach is used in the present work to predict the energies of formation of binary and ternary structures of  $\gamma$ -TiAl alloys similar to the ones investigated experimentally in [8]. Considering temperature effects in DFT is difficult as especially the contributions from lattice vibrations and electron vibrations to the entropy can only be calculated with high computational efforts [13]. Nevertheless, it is possible to consider the contribution of configurational entropy, which is used in the present work to acquire some hints about the situation at elevated temperature.

## Methods

The DFT calculations were performed using the software ABINIT in its version 8.4.3 [14,15]. For all calculations and elements optimized norm-conserving Vanderbilt pseudopotentials with an energy cut-off of 75 Ha ( $\approx 2000$  eV) and a Perdew-Bruke-Ernzerhof general gradient approximation (GGA) functional [16] were used. To consider possible magnetic effects due to the presence of Fe and Cr in the ternary compounds the calculations of these ternary systems were done spin polarized. The self-consistent field cycles were converged to an energy difference  $< 10^{-6}$  Ha. In all calculations a Monkhorst-Pack grid k-point mesh was used with a k-point length of at least 32 Bohr as well as a thermal smearing of 0.001 Ha. All structures were fully relaxed using the Broyden-Fletcher-Goldfarb-Shanno minimization until a convergence of  $< 5 \times 10^{-5}$  Ha/Bohr was reached.

The energies of the different binary (Ti and Al) and ternary (Ti, Al and one of the elements Ta, Nb, Mo, Fe or Cr) compositions of the bcc structure ( $\beta$ -phase) and B2 structure ( $\beta_0$ -phase) are calculated using SQSs. These SQSs were constructed using the mcsqs programme of the ATAT software package [17] and pair interactions up to 5th and triple interactions up to 2nd neighbours were considered. The SQSs consisted of eight atoms except for the SQS representing the bcc structure with the composition 50 at.% Ti and 50 at.% Al where the pair and triple interactions could only be achieved with a 16-atom SQS. For the construction of the SQSs of the B2 structure it was assumed that the majority element (either Ti or Al) fully occupied one sublattice while the second sublattice was shared by the minority element, the excess atoms of the majority element and if present the ternary alloying element. Fig. 1 shows an example of a SQS representing a bcc structure with 75 at.% Ti and 25 at.% Al.

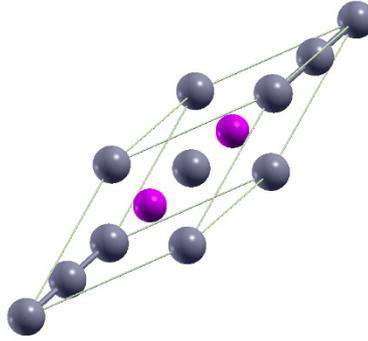


Fig. 1: Example of an 8-atoms SQS representing a 75 at.% Ti (grey) and 25 at.% Al (purple) bcc structure

The energy of formation of the different structures is calculated according to the following formula  $E_F = E(B2/bcc Ti_xAl_yX_z) - xE(Ti) - yE(Al) - zE(X)$  with  $E(B2/bcc Ti_xAl_yX_z)$  being the energy of the compound of interest and  $E(Ti)$ ,  $E(Al)$  and  $E(X)$  being the energies of Ti, Al and X in their respective ground states ( $X$  being the ternary alloying element Ta, Nb, Mo, Cr or Fe if present). To evaluate the Gibbs free energy at temperature  $T$  the configurational entropy  $S_{conf}$  was considered using  $G = E_F - TS_{conf}$ .  $S_{conf}$  was calculated with a sublattice model:  $S_{conf} = R \sum_m f \sum_i x_i \ln x_i$ ,  $m$  being the number of sublattices,  $f$  being the site fraction of one sublattice and  $x_i$  being the content of element  $i$  on that sublattice. Similar sublattice models are used to calculate configurational entropies in CLAPHAD simulations [10].

## Results and Discussion

In Fig. 2 the energies of formation for the bcc structure (disordered) and the B2 structure (ordered) are plotted over the Al content. That pure Ti and pure Al have positive energies of formation represents the fact that their ground state structures are not bcc but hcp for Ti and fcc for Al. Thus, the positive energies of formation indicate that hcp or fcc are more stable. Also for pure Ti and pure Al there is no difference between the ordered and disordered structure as both sublattices in the ordered B2 structure are completely occupied by either Ti or Al. Also, it is obvious that for the range of Al-contents of interest with respect to  $\gamma$ -TiAl alloys, i.e. between 25 and 50 at.% Al, the energy of formation of the ordered B2 structure is always lower than the one of the disordered bcc structure. The situation is only changed for 75 at.% Al possibly due to the fact that  $Al_3Ti$  has the  $D0_{22}$  structure [6]. Thus, it may be energetically unfavourable to force it in an ordered B2 structure. The fact that for 25 at.% and 50 at.% Al the ordered B2 structure has the lower energies of formation is in contradiction to the measurements in [8] which did not find any ordered  $\beta_0$ -phase with B2 structure in binary  $\gamma$ -TiAl alloys with Al contents between 39 to 45 at.%. Thus, it can be deduced, because the DFT calculations represent the situation at 0K, that the ordered structure is always favoured as long as no temperature effects are taken into account. The energy of formation for the ordered phase is lower by 2766 J/mol and 2669 J/mol for 25 and 50 at.% Al, respectively.

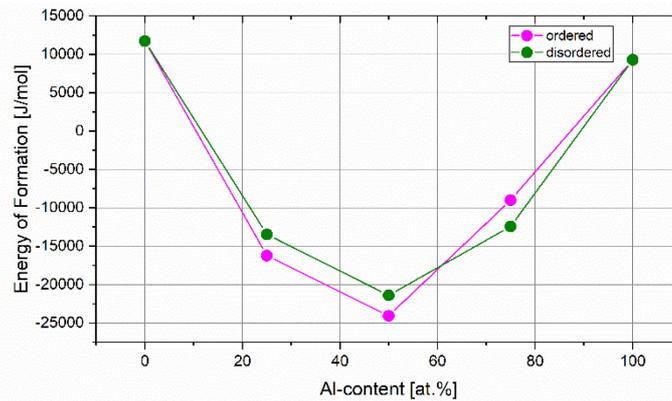


Fig. 2: Energy of formation for bcc (disordered) and B2 (ordered) structure with different contents of Al – line between the data points is to guide the eye

Nevertheless, the disordered structure allowing to distribute the two atomic species more randomly on all lattice sites should exhibit a larger entropy and thus become thermodynamically more favourable with increasing temperature. To get an idea whether this contribution of entropy could be sufficiently high to stabilize the disordered bcc structure versus the ordered B2 structure, the Gibbs free energy of both structures for different contents of Al were calculated for a temperature of 1400 °C. This temperature was chosen based on the binary Ti-Al phase diagram because in the medium Al concentration range interesting for  $\gamma$ -TiAl alloys other phases than  $\beta$  or  $\beta_0$  are stable at lower temperatures. From Fig. 3 it is obvious that for 25 at.% of Al the disordered structure exhibits a slightly lower Gibbs free energy while the difference is most pronounced for 50 at.% Al. Thus, the difference in configurational entropy is sufficiently large to stabilize the disordered bcc structure. Actually for 25 at.% Al the Gibbs free energy for the bcc structure is lower for temperatures of 1269 °C and above while it is already lower for temperatures of 190 °C and above for 50 at.% Al.

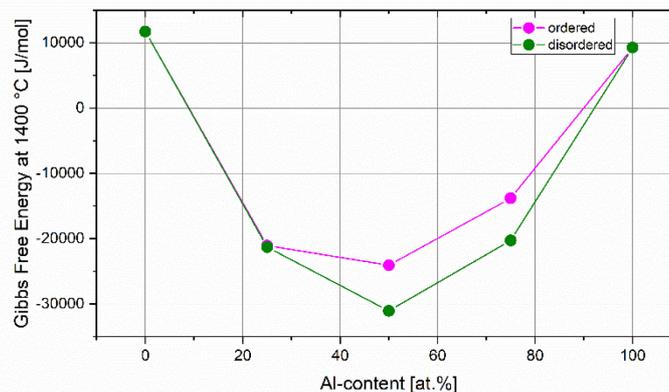


Fig. 3: Gibbs free energy at 1400 °C for bcc (disordered) and B2 (ordered) structure with different contents of Al – line between the data points is to guide the eye

It has to be noted that the concept used here to calculate the entropy is rather simplistic only considering configurational entropy, filling one sublattice in the ordered structure completely with the majority element only allowing mixing on the second sublattice. Therefore, the entropy for the ordered structures is probably underestimated. Nevertheless, it is proved that contributions from entropy at the temperatures in question can be sufficiently large to overcome the lower energy of formation of the ordered B2 structures and hence disordered bcc phase is present in the binary Ti-Al system.

Besides finding evidence for an ordered B2 structure in the binary Ti-Al system in [8] also the effects of different ternary alloying elements on the ordering and disordering between the B2 and the bcc structure were investigated. It was found that for additions of 2 at.% of Ta, Nb, Cr, Mo and Fe no ordered phase with B2 structure was present if Ta or Nb were added but an ordered B2 structure could

be found in Cr, Mo and Fe containing specimens. It is prohibitive in DFT to consider such low contents of alloying elements as 2 at.% because the necessary large supercells would take too long to calculate. Thus, SQSs representing the B2 structure and consisting of 50 at.% Ti, 25 at.% Al and 25 at.% X (X=Ta, Nb, Cr, Mo and Fe) were constructed with Ti fully occupying one and Al and X sharing the second sublattice. For comparison SQSs representing the bcc structure were used with Ti, Al and X in the same concentrations as in the B2 structure but now free to assume all lattice positions. In Figure 4 the energies of formation for the ternary ordered B2 and disordered bcc structures are plotted. Again, except for the Ta containing compound, the energies of formation of the ordered structures are always lower compared to the ones of the bcc structures predicting that at 0 K the B2 structure should be more stable. Nevertheless, a number of conclusions can be drawn and related to the experimental results of [8]. When only considering the energies of formation of the B2 structures it is evident that the ternary compounds containing Mo and Fe exhibit the lowest energies of formation. These are the two alloys, which also showed ordered B2-phase in the experiments while the Ta- and Nb-containing compounds, where no ordered B2 structure was detected experimentally, have also significantly higher energies of formation. If the energy of formation of the disordered bcc and ordered B2 structure is compared the stabilization of the ordered B2 structure by Mo and Fe becomes even more pronounced. The energies of formation of bcc  $\text{Ti}_{0.5}\text{Al}_{0.25}\text{Mo}_{0.25}$  and  $\text{Ti}_{0.5}\text{Al}_{0.25}\text{Fe}_{0.25}$  stay nearly on the same level while the energies of formation for the corresponding B2 structures decrease. This makes a transformation from the disordered bcc to the ordered B2 structure energetically even more favourable.

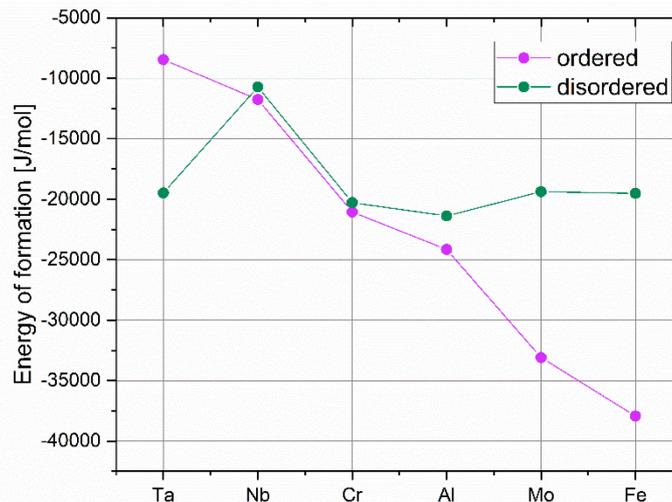


Fig. 4: Energies of formation for B2 (ordered) and bcc (disordered) structures of  $\text{Ti}_{0.5}\text{Al}_{0.25}\text{X}_{0.25}$  compounds (X = Ta, Nb, Cr, Al, Mo, Fe)

In Fig. 4 also the energies of formation for the B2- $\text{Ti}_{0.5}\text{Al}_{0.5}$  and bcc- $\text{Ti}_{0.5}\text{Al}_{0.5}$  compounds are plotted. These can be used as a hint whether we should expect to find an ordered or disordered phase. From the investigations of the binary Ti-Al system it is already known that no ordered structure is present there. Thus, it is reasonable to assume that all compounds which exhibit an even higher energy of formation than  $\text{Ti}_{0.5}\text{Al}_{0.5}$  should not form an ordered phase at higher temperatures in  $\gamma$ -TiAl. Following this line of argumentation, we expect to find no ordered B2 structures for the ternary compounds  $\text{Ti}_{0.5}\text{Al}_{0.25}\text{Ta}_{0.25}$ ,  $\text{Ti}_{0.5}\text{Al}_{0.25}\text{Nb}_{0.25}$  and  $\text{Ti}_{0.5}\text{Al}_{0.25}\text{Cr}_{0.25}$ . This corresponds with the experimental results in [8] except for Cr. While it is beyond the scope of this work, a possible explanation for the unexpected behaviour of the Cr containing compound could be that Cr distributes differently between the sublattices as assumed here. To prove this, calculations with Cr being located on the Ti sublattice or distributing evenly between the two sublattices would be necessary.

## Conclusions

- DFT calculations were used to confirm experimental results about ordering and disordering of the  $\beta/\beta_0$ -phases in  $\gamma$ -TiAl alloys
- The DFT calculations confirm the stability of the disordered  $\beta$ -phase in the binary Ti-Al system if configurational entropy is considered
- DFT calculations predict a stabilization of the B2-structure by Mo and Fe in accordance with experimental results while the same effect of Cr could not be confirmed.

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