Chapter 7

Conclusion

7.1 Summary

Atomistic modelling of solid-solid phase transformations is a challenging task. This challenge shows in the need for larger simulation systems and dependence on long time scales in relation to the precision needed to resolve its processes. This work is dedicated to study the kinetics of such solid-solid phase transformations between very different phases, one of which is a complex phase from the family of topologically close-packed phases.

This creates the need for proper identification of the crystal phase an atom site is belonging to on a level local and precise enough to resolve the interface. The identification further has to be able to identify complex phases, like the TCP phases. As many local analysis methods exist that are able resolve an interface between two different crystal phases, none of them is further able to distinguish and identify topological close-packed phases. For this reason a new analysis method was developed to support the analysis of material simulations in this work.

A detailed explanation of this new analysis method was given in this work. The method uses the information of local environments encoded in coordination polyhedra to create topological fingerprints that can be used to characterise and distinguish crystal phases in a simulation. The identification of the coordination polyhedra is done by determining the atoms belonging to the local environment, using a maximum gap or Wigner-Seitz like approach, and then comparing it with other coordination polyhedra from a reference database, assigning the best matched reference polyhedron to the local environment. Analysing the coordination polyhedra results along closed hop sequences creates fingerprints to characterise the structure around an atom. This is done through setting the number of hops in the closed hop sequence. Many crystal phases can be identified using a small number of hops. Complicated structures with similar local environments, meaning the difference is only seen on larger scales, need higher order fin-
gerprints. One example for such phases needing higher order are the Laves phases.

This analysis method has been inspected on test simulations in copper and later proved its usefulness with the analysis of the main simulations. The topological fingerprints are used to analyse dynamical simulations with complex TCP-phases identifying the structures present, which no other known analysis is capable of at the moment.

The modular use of fingerprints of different order makes it possible to distinguish crystal phases that have a nearest neighbour structure that is not sufficient for the identification. This increases the range of application of this approach from other analysis methods, like common neighbour analysis and Steinhardt parameters. These analysis methods are restricted to the first coordination shell, thus limiting themselves. Calculating the neighbour shells with methods like the maximum gap and Wigner-Seitz approach, makes the simulation independent from accurately pre-set cut-offs but also increases computational effort. The independence of pre-set cut-offs improves the analysis of systems with multiple phases. The determination of the coordination polyhedron vertices and the coordination number is crucial to this method of structure analysis, as the polyhedron comparison is only conducted on reference polyhedra of the same coordination.

Methods to track and identify point defects were further introduced. The methods work with knowledge of the ideal structure, which can be calculated with the structure analysis, to find the local distortions from point defects. This can be done by a mapping scheme that is no dependent on coordination polyhedra or by defected polyhedra analysis, where not the complete system has to be mapped, but the information of defective polyhedra around a point defect is used to identify the defect.

In this study, dynamic atomistic simulations have been conducted on iron chromium interfaces between the bcc and the \( \sigma \)-phase. As no studies of the iron chromium bcc to \( \sigma \)-phase is known that shows its atomic structure, it was created for the simulation. The interface was created by matching of different surfaces of bcc and fcc on another and then testing their mismatch, interface energy and behaviour at MD simulations with different temperatures. No interface was found to behave distinctly different from the other interfaces during simulations. The interfaces with the lowest energy and low shape mismatch was determined as the FeCr bcc (001) to FeCr \( \sigma \) (001) interface. This interface has also the smallest simulation cell. This interface was further studied with akMC and MD simulations of up to 10 ns.

The akMC simulations were mainly conducted on the FeCr bcc (001) to FeCr \( \sigma \) (001) interface at \( T = 600 \) K temperature. The set-up was varied by changing the temperature to \( T = 900 \) K, adding vacancies or changing the bcc region to pure iron, to study their effects on the interface movement. The different modification did not change the interface movement behaviour. All simulations have shown a bcc growth into the \( \sigma \)-phase that could only be
stopped on the tested time scales by an interface change that rotates the \( \sigma \)-phase off-centre. This changes in the interface lowers the system energy, even though it creates an additional grain boundary. Simulations conducted with this interface at elevated temperatures show that it does not move quickly at higher temperatures either.

Another conclusion from the akMC simulations is the ineffectiveness of the method at the FeCr bcc (001) to FeCr \( \sigma \) (001) interface with an EAM potential. From the behaviour of the bcc growth in MD and akMC it is clear that the growth is a rare event process with long unchanging phases interrupted by very fast phase transformations. This is due to the problem that the processes found during the search in akMC include many processes that are more akin to thermal fluctuations than a real changing process. This shows that the energy surface at the minima must be rugged with many low energy barriers in it. This makes the superbasin, a set of local minima that are very similar in structure and energy and are only separated by very low energy barriers, the actual minima in phase space that are sought after and processes between superbasins, the processes expected from the akMC method. As the only current way to find the processes in akMC is to run through them and group them together afterwards, a better understanding of the inter- and intra superbasin processes is desired to improve the superbasin search and increase the effectiveness of process searches in this and possible other systems.

To get a better understanding of the processes and the system, searches for correlation in the simulation have been conducted. The correlation search was conducted for all processes found in the akMC simulation, even the processes not chosen to advance the dynamics of the system. In the data that were acquired that way, obvious correlations between volume and coordination number were found as well as a strong correlation between volume and coordination changes with an average of \( \approx 5\text{Å}^3 \) per coordination number change in the region of nine-fold to seventeen-fold coordination. Correlations between the polyhedron volumes and energy change were further found. They were found on a macroscopic scale for all atoms at the same coordination number and on a microscopic scale for all atoms at the same coordination number experiencing the same coordination number change. Both correlations show a decrease in energy change with an increase in polyhedron volume change. Further analysis along transformation trajectories show strong correlations of the atomic energies to the coordination of the atom and its neighbours. The dependence of the macroscopic volume change to the coordination and the energy correlation with the coordination along trajectories lead to a strong role of coordination effects in the potential, which in part also explains the favouring of the bcc phase, which has a higher average coordination (14) than the \( \sigma \)-phase (13.46). These coordination effects proposes effects of the effective volume available to atoms, as higher coordination suggest a larger polyhedron and thus larger volume,
while larger coordination of neighbours suggest larger volumes associated to the neighbours, which impedes on the volume of the atom. The energy change from microscopic volume changes further reinforces the effective volume dependency. The higher effective volume of bcc compared to the $\sigma$-phase in the simulations can be achieved as the volume of the simulation cell and the number of atoms are constant throughout the simulations.

### 7.2 Outlook

The dynamics of the improved interface at iron chromium interfaces between bcc and $\sigma$ should be further studied. As the interface creation has not been too elaborate to leave time for dynamical simulations, a deeper study on the creation of the interface is also recommended. Examining the effect of different orientations and translations of the surfaces at the interface are assumed to improve the results strongly as the occurrence of the improved interface in simulations suggests. Research on the dynamics of then newly found interfaces, as well as the improved interface found in this work, can be conducted to gain better results on the processes.

The processes are another topic that needs further investigation. As this work only started to determine correlations of the transformation processes during atomistic simulations, further study on the correlations are suggested to get a better understanding of the transformation processes. With a full understanding of correlations at the processes a description of the transformation might be possible in a way to find an easily calculated aspect of the transformation that will help bridge the superbasin problem encountered in this work. This problem severely slows studies on interface movement with the akMC method, making studies of interface mobilities and nucleation growth impractical.