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Thermodynamic modelling of the general NiAs-type structure: A study of first principle energies of formation for binary Ni-containing B8 compounds

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ABSTRACT

Energies of formation of binary Ni-containing compounds with NiAs (B8)-type structure were calculated using ab-initio density functional theory. Structural relaxations and calculation of the total energies of the binary structures NiX_2 as CdI_2-type structure, NiX as NiAs-type structure and Ni_2X as Ni_2In-type structure (with X= Al, Ga, In, Si, Ge, Sn, As, Sb, Bi, Se, Te) were done using the projector augmented wave (PAW) method with a generalised gradient approximation (GGA).

Overall, the calculated values are in good agreement with comparable experimental literature data. General trends of the lattice parameters and the energies of formation are discussed in detail. Nearly all of the calculated compounds are thermodynamically stable compared to the elements at zero Kelvin, although not all of them are present in the equilibrium phase diagrams.

According to a recent investigation of the system Ni–Sn–Te, continuous solid solutions from CdI_2-type, over NiAs-type, up to Ni_2In-type regions are possible. Hence, a modified sublattice model according to the compound energy formalism within Calphad is proposed to give this possibility consideration. The use of the calculated energies of formation at 0 K as endmember energies within this model is discussed.

1. Introduction

The improvement of existing and development of new materials plays an important part in industry today. To precisely produce alloys with specific properties, the knowledge of the according phase diagrams is crucial. Nowadays, alloys are getting more and more complex, consisting of many different components. Thus, a solely experimental approach to investigate the desired phase diagrams is hardly possible any more.

Different approaches were developed to support or replace experimental investigations. One of them is the Calculation of Phase Diagrams (Calphad) method. It is a very important tool to calculate equilibrium conditions and thermodynamic properties of multicomponent alloys. Kroupa [1] gave a recent review over the method with special focus on the development of thermodynamic databases.

As it is a semi-empirical approach, input data are necessary for an accurate description of alloy systems. Besides information from experimental investigations, especially calculations are getting more important for the implementation of data into Calphad models. Already Ansara et al. [2] discussed the importance of first principle predictions for Calphad modelling in 1997. From then on, many authors dealt with the incorporation of first principle calculations into Calphad modelling. Burton et al. [3] and Liu [4] gave detailed overviews and discussed the use of many different calculated properties, e.g. equations of state, bulk moduli, elastic constants and formation energies, for thermodynamic modelling. More specialised reports were given by Sob et al. [5] about ab-initio electronic structures for systems with complex phases and Körmann et al. [6] about thermodynamic modelling of magnetic and chemical order-disorder transitions. Pettifor [7] discussed the importance of ab-initio electronic structure calculations not only for the Calphad-approach, but also for other fields in materials modelling (Engel–Brewer theory, 2γ-state hypothesis and Griffith criterion). Considering some of the recent research papers concerning Calphad modelling, e.g. Refs. [8–11], it is now state of the art to combine first principle calculations with experiments to develop physically meaningful thermodynamic models.

The main field of application for first principle calculations in thermodynamic modelling, which is also the focus of the current study, is the calculation of energies of formation of endmembers. They are needed to accurately describe the boundaries of phases

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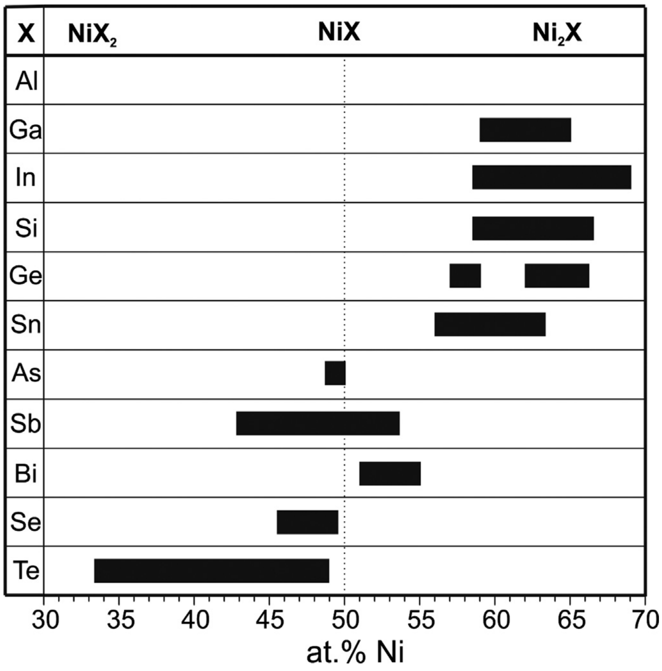

Fig. 1. Occurrence and homogeneity range of some NiAs compounds in the corresponding binary equilibrium phase diagrams (maximal extension of homogeneity range).

with homogeneity ranges. These phases are modelled according to the compound energy formalism (CEF) [12] within the Calphad approach. Thereby, different sublattices, according to the atomic positions of the structure, are established and filled with the respective atoms. The boundaries of the homogeneity ranges are defined by the endmembers. They can be determined experimentally, if the structures are stable. Often, such endmembers are metastable or unstable and do not exist in reality. Thus, the endmember energies have to be estimated or better calculated using first principle methods.

One widespread structure type of intermetallics that forms broad homogeneity ranges in the binary and extended solid solutions in the ternary is the general NiAs type (Strukturbericht designation: B8). Phases of this structure type are composed of transition metals T and main group elements X out of the 13th to 16th group, forming $T_{1\pm x}X$ structures. Such phases are present in many alloy systems that are applied in various fields. Kjekshus and Pearson [13] gave an early overview about binary NiAs phases and their specific properties. Up to now a three-sublattice model was used for the description of NiAs phases and their broad non-stoichiometry, originally proposed by Waldner and Ipser [14] during their thermodynamic optimisation of the Ni–In system. In all cases, it was assumed that the X-sublattice remains undisturbed and the non-stoichiometry is due to vacancies on the T-sublattices. This model is very well supported by experimental evidence, although there are no theoretical calculations to support it. Ehrlich [15] gave an early review about CdI_2 and NiAs structures and suggested the existence of vacancies due to pycnometric density measurements. Ellner [16,17] discussed the lattice parameter variations of NiAs compounds in detail. The trends he found, like volume decrease with decreasing transition metal content, argue for a vacancy-based defect mechanism. Many different studies on NiAs compounds [18–23] confirm this mechanism. Not only lattice parameter variations, but especially X-ray diffraction measurements in combination with Rietveld refinements, used in some of these studies, are able to distinguish between vacancies and anti-site defects.

Therefore, although a few anti-site defects cannot be fully excluded, it is certainly not useful to consider them for Calphad calculations, as a corresponding model would have too many endmembers. It is the scope of this work to modify and extend the sublattice model for NiAs phases in order to be able to describe the broad homogeneity ranges in ternary NiAs phases and to be able to use calculated endmember energies for Calphad-type optimisations. For further explanations about the structure type and the modified sublattice model see Section 2.

Phases with B8 structure show up in many systems of technological relevance. A large sphere of interest is contact chemistry for compound semiconductors. There, NiAs phases are present as intermediate layers at the interface between III–V semiconductors and transition metals, which are used as contact layers [24]. Hence, ternary III–V–T systems (with T=Ni, Pd, Pt) were in focus of research for many years [25,26]. NiAs phases containing Fe, Mn or Cr are interesting because of their magnetic properties [27–30]. Especially Mn–As compounds with Sb [31] or Fe [32] are discussed as materials for magnetocaloric refrigeration. Li-ion batteries are a steady field of research during the last years, where phases derived from NiAs structures are discussed as materials for intermetallic insertion electrodes [33].

Ternary systems containing noble metals that form phases with NiAs structures have been investigated because of their catalytic properties. Especially Ni–Pt–Sn alloys are widely discussed as electrocatalysts for ethanol [34–36] and ethylene glycol [37,38] oxidation in fuel cells. Furthermore, many higher order systems that are studied in the context of joining technologies will show the formation of NiAs-type structures and solid solutions, such as, systems for transient liquid phase bonding (TLP) [39–42] and lead-free solders [43,44].

As can be seen from this brief listing of the most important application areas, a wide variety of NiAs compounds exist. Thus, the current study focuses on compounds with only Ni as transition metal T in combination with several main group elements X (X=Al, Ga, In, Si, Ge, Sn, As, Sb, Bi, Se, Te). These compounds are of particular interest, since Ni and Ni alloys have many technological applications. Moreover, most of the corresponding binary phase diagrams show NiAs phases. Fig. 1 gives an overview of the existing NiAs compounds in Ni–X systems and their homogeneity ranges.

Within this work, the energies of formation of the named compounds in the different NiAs-type boundary structures are calculated using ab-initio density functional theory. The obtained values will serve as endmember energies for several Calphad optimisations.

2. Structural characterisation and modelling of the general NiAs-type structure

The general NiAs structure is based on a hexagonally close-packed arrangement of main group elements X out of the 13th to 16th group. Such a hexagonal close-packed lattice contains one octahedral and one trigonal-bipyramidal (or double-tetrahedral) hole per lattice site. A characteristic of the NiAs structure family is its ability to fill these holes partially or completely with transition metals. In case of the stoichiometric NiAs structure the octahedral holes are filled completely by transition metal atoms T, forming 1:1 structures TX (Strukturbericht designation: $B8_1$). The additional filling of the trigonal-bipyramidal holes leads to structures of the form $T_{1+x}X$, with $0 < x \leq 1$. If these holes are completely occupied the Ni_2In structure-type (Strukturbericht designation: $B8_2$) is reached. On the other hand, a transition metal deficit leads to vacancies at the octahedral positions, forming structures $T_{1-x}X$, with $0 < x \leq 0.5$. By ordering of these vacancies in every other layer perpendicular to the *c*-axis, the CdI_2-type structure is