Structural stability of intermetallic phases in the Zr–Sn system

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A thermodynamic description of the intermetallic compounds in the Zr–Sn binary system has been obtained using total energy calculations by means of the Vienna *ab initio* simulation package. Our calculations show that hexagonal compounds Zr_5Sn_4 and Zr_5Sn_3 are the most stable phases in the Zr–Sn binary system. Their high stability is found to be due to hybridization of the Sn 5p with Zr 4d electronic states. Based on the calculated energies, the conclusion is made that Zr substitution on the Sn sites takes place in the Zr Sn phase, which accounts for the unusual stoichiometry of this Cr_3Si structure type compound.

Zirconium alloys with 1.2–1.7 % Sn, and small amounts of other transition elements, have been used for many years as materials for fuel cladding in nuclear reactors. Nevertheless, some uncertainties still exist concerning the Zr–Sn binary system.

The experimental data about this system are scarce. Studies of the intermetallic compounds in the Zr–Sn system have been performed by McPherson and Hansen [1], Gran and Anderson [2], Luo and Vielhaber [3], Naik and Banerjee [4], Kwon [5,6], and Arias [7]. In general they agree about the existence of Zr_4Sn, Zr_5Sn_3, and $ZrSn_2$ compounds. However, the existence of the compound Zr_5Sn_4, first reported by Kwon [5,6,8], still remains in doubt. Furthermore, the discrepancy between the stoichiometry of the Zr_4Sn phase and its crystal structure (A15, Cr_3Si prototype) has not been clarified yet.

McPherson and Hansen [1] first studied the Zr–Sn system and reported a tetragonal phase with stoichiometry Zr_4Sn. Later, Gran and Anderson [2] and Naik and Banerjee [4] concluded from their X-ray studies that this compound had a cubic A15 structure with the ideal Zr_3Sn stoichiometry. On the other hand, Luo and Vielhaber [3] have shown that the phase is stable at the Zr_4Sn composition, but still it has the A15 structure. Kwon [5] suggested that the deviation from the ideal A15 stoichiometry in the Zr_4Sn compound could be due to one of the two possible kinds of structural defects, either Sn vacancies,

$Zr_3(Sn_{0.75}Va_{0.25})$, or Zr anti-site defects on the Sn sublattice, $Zr_3(Sn_{0.8}Zr_{0.2})$. There are many other cases, such as $AsCr_4$, Cr_4Pt, $AuTa_5$, *etc.*, where the composition of an A15 compound deviates from the ideal stoichiometric composition of primary (A_3B) and secondary (A_7B and A_5B_3) atomic ordering within the A15 lattice framework [9].

The intermetallic compound Zr_5Sn_3 with the hexagonal Mn_5Si_3 prototype structure was first reported by McPherson [1]. Later, Gran and Anderson [2] performed X-ray diffraction and identified two phases of the Zr_5Sn_3 type, hexagonal Zr_5Sn_3' and Zr_5Sn_3'', the latter with a larger cell volume and a higher Sn content. Abriata et al. [10] published a provisional Zr–Sn phase diagram and discussed a possible intermetallic compound Zr_5Sn_4, without including it in the phase diagram. Several papers [5,6,11], based on X-ray diffraction and scanning electron microscopy studies, reported the existence of two compounds with closely related crystallographic structures, Zr_5Sn_3 (Mn_5Si_3 prototype structure) and Zr_5Sn_4 (Ti_5Si_4 prototype structure). Kwon and Corbett note in their paper [5] that phases with the Mn_5Si_3 prototype may incorporate a variety of interstitial atoms into the center of confacial octahedra, which form a chain along the *z*-axis. Thus, a full occupancy of the interstitial sites in Zr_5Sn_3 phase by Sn may enlarge the hexagonal cell to form Zr_5Sn_4. Further, in Refs. [5,6] it was proposed that the these two compounds exist and are stoichiometric at temperatures up to ∼1373 K, but at higher temperatures, due to their structural similarities, the two compounds merge into a single phase, Zr_5Sn_{3+x}, with $0 \leqslant x \leqslant 1$.

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In cases where the experimental information is incomplete, modern first principles methods allow one to calculate the thermodynamic properties of materials from basic quantum mechanical principles. In the present study we use first-principles calculations to resolve the two problems mentioned above, namely, to verify at zero temperature the thermodynamic stability of Zr_5Sn_4 compound and to determine the type of structural defects in the Zr_4Sn compound, relative to the A15 structure.

The present total energy calculations are performed using the Vienna *ab initio* simulation package (VASP) [12] in which the interaction between the ions and electrons is described by the projector augmented-wave (PAW) method, proposed by Blöchl [13] the total energies were calculated employing the generalized gradient approximation [14]. The calculations include 12 valence electrons for Zr, with the semicore 4s and 4p states, and a plane-wave cutoff energy of 230 eV. For Sn, 14 valence electrons are used, including the semicore 4d electrons, with a plane-wave cutoff energy of 241 eV. The reciprocal space sampling was performed with a $9 \times 9 \times 9$ **k**-point grid for the Zr_5Sn_3 (Mn_5Si_3 prototype structure) and the Zr_5Sn_4 (Ti_5Ga_4 prototype structure), which both have the same hexagonal symmetry. Grids of $9 \times 9 \times 9$ and $8 \times 8 \times 8$ size, respectively, were used in the Brillouin zone sampling for the face-centered orthorhombic structure $ZrSn_2$ and for Zr_4Sn in the A15-type cubic structure.

The total energies of the different compounds were calculated within the fully relaxed geometry, including the volume of the supercell and the internal atomic positions. The enthalpy of formation, ΔH^{form}, was extracted from the total energy minimum by subtracting the concentration-weighted minimum total energies of pure hexagonal close-packed Zr and body-centered tetragonal Sn:

$$\Delta H^{form}_{Zr_{1-c}Sn_c} = E^{min}_{Zr_{1-c}Sn_c} - (1-c)E^{min}_{Zr} - cE^{min}_{Sn}.$$

In Figure 1 we display the calculated enthalpy of formation for different compounds and alloys in the Zr–Sn binary system. Our calculations show that the Zr_5Sn_4 compound is stable, relative to compounds Zr_5Sn_3 and $ZrSn_2$. The Zr_5Sn_4 and Zr_5Sn_3 compounds belong to the same crystallographic space group. From the crystallographic information listed in Tables 1
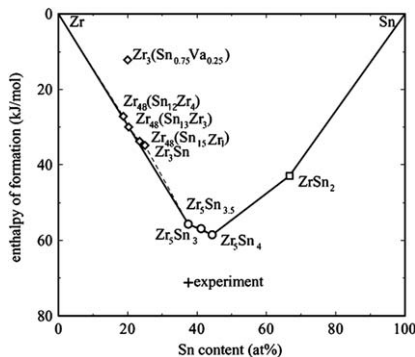
Table 1. Crystallographic data of Zr_5Sn_4, $Zr_5Sn_{3.5}$, and Zr_5Sn_4; space group P6$_3$/mcm, No.193

Site	Position	X	Y	Z	Site occupancy		
					Zr_5Sn_3	$Zr_5Sn_{3.5}$	Zr_5Sn_4
Sn1	2b	0	0	0	0	0.5	1
Sn2	6g	x_{Sn}	0	1/4	1	1	1
Zr1	4d	1/3	2/3	0	1	1	1
Zr2	6g	x_{Zr}	0	1/4	1	1	1

Table 2. Crystallographic data of $ZrSn_2$; space group Pm3m, No.70

Element	X	Y	Z	Site occupancy
Zr (8a)	0	0	0	1
Sn (16e)	x_{Sn}	0	0	1

and 2 one can conclude that Zr_5Sn_3 is identical to Zr_5Sn_4 except for the site Sn1, whose occupancy is zero in the former case. Let us take the line drawn between those two compounds as the ground state at 0 K and consider an intermediate case, $Zr_5Sn_{3.5}$, where the occupation of the Sn1 site is 0.5, see Table 1. Note that the calculated enthalpy of formation of this intermediate compound is very close to the ground state line in Figure 1. Based on this fact, it is can be expected that at high temperatures the Zr_5Sn_4 and Zr_5Sn_3 phases will merge into a single phase Zr_5Sn_{3+x} with $0 \leqslant x \leqslant 1$ as it was suggested by Kwon [5] and shown in Figure 2. Also, the crystallographic structure of the Zr_5Sn_{3+x} phase (see Fig. 3) suggests that in the presence of a third element Z (O, C, Fe, *etc.*) in the alloy, it is possible to form ternary compounds of the type $Zr_5Sn_{3+x}Z_{1-x}$.

In Table 3 we compare the calculated enthalpies of formation with the enthalpies of formation evaluated using Miedema's semi-empirical theory of macroscopic atom [15]. Although there are substantial differences (up to 30%) between the calculated and evaluated values of the enthalpy of formation, both these methods predict the same qualitative trend of phase stability. The quantitative differences between the calculated and evaluated enthalpies of formation are caused by the approximations used in both methods, and are within the expected range.

Experimentally, the enthalpy of formation was measured [16] only for the hexagonal Zr_5Sn_3 compound. The experimental value -71.2 kJ/mol [16] falls in between the calculated value and the estimated value of the energy of formation for Zr_5Sn_3, see Table 3. The *ab initio* calculated energies of formation of all the
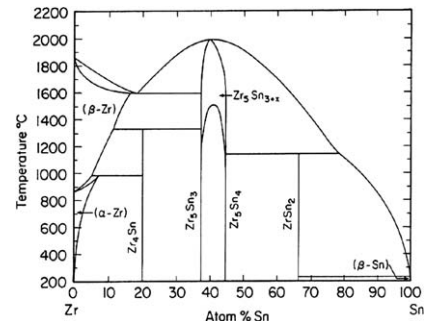

Figure 1. Enthalpy of formation of the intermetallic compounds in the Zr–Sn binary system.

Figure 2. Phase diagram of the Zr–Sn binary system, by Kwon and Crobett [5].
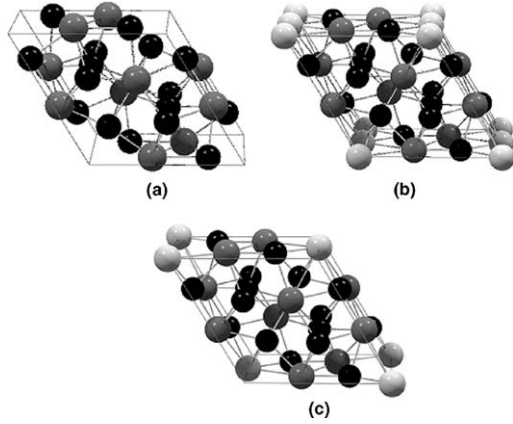
Figure 3. Unit cells of Zr_5Sn_3 (a) and Zr_5Sn_4 (b). The black spheres are Zr atoms and the grey spheres are Sn atoms. In panel (b) the white spheres represent the extra Sn atoms placed in the interstitial sites of the hexagonal Zr_5Sn_3. This configuration leads to a hexagonal structure Zr_5Sn_4 with fully occupied interstitial sites. In panel (c) the structure of Zr_5Sn_{3+x} with $x = 0.5$ is shown.

Table 3. Enthalpy of formation for the Zr–Sn intermetallic compounds

Compound	Enthalpy of formation (kJ/mol)		
	Calculated	Evaluated Miedema	Assessed (300 K)
$Zr_3(Sn_{0.75}Va_{0.25})$	−12.186		
$Zr_{48}(Sn_{12}Zr_4)$	−27.136		
$Zr_{48}(Sn_{13}Zr_3)(Zr_4Sn)$	−29.940	−48	−41.89
$Zr_{48}(Sn_{15}Zr_1)$	−33.750		
Zr_3Sn	−34.834		
Zr_5Sn_3	−55.670	−80	−73.23
$Zr_5Sn_{3.5}$	−56.902		
Zr_5Sn_4	−58.490	−85	−76.66
$ZrSn_2$	−42.905	−67	−61.02

Zr–Sn intermetallic compounds, together with the measured enthalpy of formation of Zr_5Sn_3 [16] as well as with other experimental data [1,5–7], have been used in a recent thermodynamic assessment [17] of the Zr–Sn binary system using the Thermo-Calc software [18]. In order to combine the calculated and experimental data into a single data set, which describes the relative stability of all the intermetallic phases in the Zr–Sn system, the *ab initio* calculated enthalpies of formation have been rescaled with respect to the only experimental value [16] available for the present binary system. Furthermore, the *ab initio* derived qualitative information on the constitution of 'non-stoichiometric' phases, Zr_4Sn and Zr_5Sn_{3+x}, has been put into thermodynamic models of these phases. Thus, the conclusion about low-temperature stability of Zr_5Sn_4 compound has been crucial for the development of the model for the Zr_5Sn_{3+x} phase, which is described as a single phase above 1373 K and with two composition sets, Zr_5Sn_3 and Zr_5Sn_4 separated by a miscibility gap, below 1373 K. In Ref. [17], the non-stoichiometry of the A15 phase was experimentally verified to be due to Zr substitutional defects in the Sn sublattice. Also the Zr_5Sn_4 compound was experimentally confirmed as well as the

miscibility gap. The final, optimized values of the enthalpy of formation of Zr–Sn binary compounds, derived as a result of the phase diagram assessment [17] using Thermo-Calc are listed in Table 3.

In order to understand the very negative enthalpy of formation (and the high melting point) of the hexagonal Zr_5Sn_{3+x} phase, let us analyze the behavior of the calculated electronic energy spectra of the hexagonal compounds with $x = 0$, 0.5, and 1. Figure 4 shows the electronic density of states (DOS) for Zr_5Sn_3, $Zr_5Sn_{3.5}$ and Zr_5Sn_4. The main contributions to the DOS come from the 5p-states of Sn and from the 4d-states of Zr, which form the familiar picture of hybridized p–d states, similar to that in the binary refractory compounds formed by transition elements of group IVA (Ti, Zr, Hf) with elements of group IVB (C, Si). This p–d hybridization is characteristic of strong covalent bonding between Zr and Sn, and is the reason of high stability of the Zr_5Sn_{3+x} compounds. The filling of p–d hybridized bonding states gives rise to the magnitude of the enthalpy of formation, which is at a maximum for the Zr_5Sn_4 compound. Similar to other IVA–IVB compounds, the Zr_5Sn_{3+x} compounds are metallic (the density of states at the Fermi level is calculated to be non-zero) and may accommodate a considerable amount of vacancies on the sublattice by a group IVB element.

The A15 structure type frequently occurs in intermetallic phases of many transition metal alloy systems. Some of these phases, such as the Nb_3Sn compound, are of particular interest in connection with superconductivity [3]. The structure type of the Zr_4Sn compound has been established as A15 (Cr_3Si prototype), with the space group $Pm\bar{3}n$. However, this structure type requires the Zr_3Sn stoichiometry, which was suggested in some experimental studies of the Zr–Sn system [2,4]. The present calculations show that the A15 phase is unstable at the ideal stoichiometry of Zr_3Sn, which is consistent
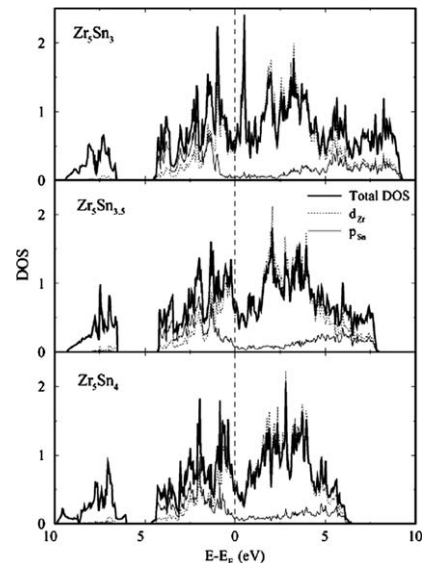

Figure 4. Electronic density of states of Zr_5Sn_x with $x = 3$, 3.5 and 4 from top to bottom, based on the hexagonal $P6_3/mcm$ crystal structure.

Table 4. Lattice parameters of the Zr–Sn intermetallic compounds

Compound	Parameter	Calculated value	Experimental Value	Ref.
Zr_4Sn	a	0.5646 nm	0.565 nm	[19]
Zr_5Sn_3	a	0.8527 nm	0.8462 nm	[20]
	c	0.5797 nm	0.5797 nm	
	x_{Sn} (6g)	0.6087	0.5991	
	x_{Zr} (6g)	0.236	0.236	
$Zr_5Sn_{3.5}$	a	0.8837 nm		
	c	0.5959 nm		
	x_{Sn} (6g)	0.613		
	x_{Zr} (6g)	0.286		
Zr_5Sn_4	a	0.8837 nm	0.8759 nm	[21]
	c	0.5959 nm	0.5797 nm	
	x_{Sn} (6g)	0.613	0.62	
	x_{Zr} (6g)	0.281	0.29	
$ZrSn_2$	a	0.9574 nm	0.9573 nm	[22]
	b	0.5662 nm	0.5644 nm	
	c	0.9962 nm	0.9927 nm	
	x_{Sn} (16e)	0.331	0.333	

with the experimentally reported stoichiometry Zr_4Sn for this phase [3,5,7].

The constitution of the Zr_4Sn phase is not well known. It has been suggested that the stoichiometry of the Zr_4Sn phase can be accounted for by two possible kinds of defects in the A15-type (Cr_3Si) structure, either by vacancies on the Sn sites [the structure may be formally described as $Zr_3(Sn_{0.75}, Va_{0.25})$] or Zr substitution on the Sn sites [formally described as $Zr_3(Sn_{0.8}, Zr_{0.2})$], the latter case being similar to the constitution of Nb_4Ge compound reported in Ref. [23].

In order to address the problem of atomic constitution of the Zr_4Sn phase, we calculated the enthalpy of formation of the $Zr_3(Sn_{0.75}, Va_{0.25})$ compound using a cubic $2 \times 2 \times 2$ supercell with 64 sites, $Zr_{48}(Sn_{12}Va_4)$. The four vacancies in the structure of the supercell were arranged into a face-centered cubic sublattice. This model of the Zr_4Sn compound, with vacancies on the Sn sites, is found to be unstable (see Fig. 1). In order to model the Zr substitution on the Sn sites we considered four model alloys, described by supercells with varying composition, $Zr_{48}(Sn_{15}Zr_1)$, $Zr_{48}(Sn_{13}Zr_3)$, and $Zr_{48}(Sn_{12}Zr_4)$. The alloy with the composition $Zr_{48}(Sn_{13}Zr_3)$ has the stoichiometry closest to that of the Zr_4Sn compound. As is shown in Figure 1, this $Zr_{48}(Sn_{13}Zr_3)$ alloy is also found to be the most stable of the model alloys energetically.

The values of the lattice parameters for each intermetallic compound were determined from the minimum of the total energy and presented in Table 4. Our theoretical results are in good agreement with available experimental data. The agreement between the experimental and calculated lattice parameter of the Zr_4Sn compound, described in our calculations as substitutional alloy $Zr_{48}(Sn_{13}Zr_3)$, additionally confirms the substitutional model of atomic structure of Zr_4Sn.

Using electronic structure calculations, we have derived *ab initio* the ground-state properties and structural characteristics of all observed intermetallic compounds in the Zr–Sn binary system. The Zr_5Sn_4 compound is found to have the most negative enthalpy of formation in the system, which allows us to conclude that this compound is stable, thus resolving the long-standing experimental uncertainty about its thermodynamic stability. The electronic structure calculations show that the high stability of the hexagonal Zr_5Sn_{3+x} phases derives from the strong covalent bonds between Zr and Sn that form as a result of hybridization between the 4d and 5p states of these two elements, respectively.

The present total energy calculations show that the A15 phase in the Zr–Sn binary system is unstable at the ideal Zr_3Sn composition. Further analysis of various atomic structure models of the A15 phase near the Zr_4Sn composition confirms the structural model by Kwon and Corbett [5], who suggested that substitution of Zr on the Sn sites is most likely to occur in the A15 type structure of this phase. The alternative model, with structural vacancies on the Sn sites, may be ruled out on the basis of the calculated total energies.

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