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The ternary system Zr–Al–Sn: isothermal section of the phase diagram at 600°C and crystal structures of the compounds

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The isothermal section at 600°C of the phase diagram of the ternary system Zr–Al–Sn was constructed in the whole concentration range, using X-ray powder diffraction and energy-dispersive X-ray spectroscopy. Limited solid solutions of the substitution type, based on the binary compounds Zr_5Sn_4 (11.1 at.% Al) and Zr_5Sn_3 (2.5 at.% Al), were observed. The crystal structure of Zr_5AlSn_3 (boundary composition of the solid solution $Zr_5Al_xSn_{4-x}$) belongs to the structure type Hf_5CuSn_3 (Pearson symbol *hP*18, space group *P*6_3*/mcm*, *a* = 8.6184(19), *c* = 5.8656(14) Å), which is a ternary variant of the structure type Ti_5Ga_4. Three ternary compounds exist at 600°C: $ZrAl_{2.682(4)}Sn_{0.318(4)}$ (structure type $TiAl_3$, *tI*8, *I*4*/mmm*, *a* = 3.98855(18), *c* = 9.0848(4) Å), $Zr_5Al_{2.71(1)}Sn_{0.29(1)}$ (structure type W_5Si_3, *tI*32, *I*4*/mcm*, *a* = 11.0530(9), *c* = 5.4071(5) Å), and $Zr_5Al_{1.68(3)-0.40(1)}Sn_{1.32(3)-2.60(1)}$ (structure type W_5Si_3, *tI*32, *I*4*/mcm*, *a* = 11.1005(9)-11.1829(12), *c* = 5.4537(5)-5.5449(6) Å). Their structures are characterized by partial ordering of Al and Sn atoms. The structure of $ZrAl_{2.68}Sn_{0.32}$ presents a cubic close-packed arrangement of atoms and is thus built up from cuboctahedra. The structures of the Zr-rich phases are built up from columns of octahedra ($Zr_5Al_{0-1}Sn_{4-3}$), and square antiprisms and tetrahedra ($Zr_5Al_{2.71}Sn_{0.29}$ and $Zr_5Al_{1.68-0.40}Sn_{1.32-2.60}$).

Zirconium / Aluminum / Tin / X-ray powder diffraction / Energy-dispersive X-ray spectroscopy / Phase diagram / Solid solution / Ternary compound / Crystal structure

Introduction

The phase diagram of the ternary system Zr–Al–Sn has previously not been investigated. The existence of a solid solution based on Zr and two ternary phases have been reported [1]: $Zr_{0.89}Al_{0.05}Sn_{0.06}$ (structure type Mg, Pearson symbol *hP*2, space group *P*6_3*/mmc*, *a* = 3.128, *c* = 5.142 Å) [2], Zr_5AlSn_3 (Hf_5CuSn_3, *hP*18, *P*6_3*/mcm*, *a* = 8.655, *c* = 5.871 Å) [3], and Zr_5AlSn_2 (Nb_5SiSn_2, *tI*32, *I*4*/mcm*, *a* = 11.181, *c* = 5.538 Å) [4]. Their cell parameters were determined and the structure types were assigned, but the positional and occupancy parameters were not refined.

The binary systems that delimit the ternary system Zr–Al–Sn have been widely studied, and the corresponding phase diagrams have been constructed in the whole concentration range [5,6]. In total, the formation and crystal structures of 12 binary aluminides have been reported in the Zr–Al system, and 4 binary stannides in the system Zr–Sn [1]. Crystallographic data of the binary compounds formed in these systems are summarized in Table 1. The binary aluminides *ht*-Zr_5Al_3 and *ht*-Zr_5Al_4 exist at high temperatures (above 1000°C). Between the binary stannides Zr_5Sn_3 and Zr_5Sn_4 with Nowotny-type structures (structure types Mn_5Si_3 and Ti_5Ga_4, respectively) at temperatures above 1300°C a continuous solid solution forms, whereas at 600°C these compounds represent two distinct phases, separated by a two-phase region. No binary compounds form in the system Al–Sn, which is characterized by the eutectic reaction L ↔ Al + β-Sn at 228°C and 97.4 at.% Sn. At the temperature of our investigation (600°C) tin is liquid, *i.e.* a liquid region is present in the Sn-rich corner of the phase diagram.

In this work we present the results of an experimental investigation of the phase equilibria in the ternary system Zr–Al–Sn at 600°C in the whole concentration range, and crystallographic parameters for the three ternary compounds, $ZrAl_{2.68}Sn_{0.32}$, $Zr_5Al_{2.71}Sn_{0.29}$ and $Zr_5Al_{1.68-0.40}Sn_{1.32-2.60}$, obtained from X-ray powder diffraction.

Table 1 Crystallographic data for binary compounds reported in the systems Zr–Al and Zr–Sn.

Compound	Structure type	Pearson symbol	Space group	Cell parameters, Å			Reference
				a	*b*	*c*	
Zr_3Al	Cu_3Au	*cP*4	*Pm*-3*m*	4.3917	–	–	[7]
Zr_2Al	$CuAl_2$	*tI*12	*I*4/*mcm*	6.854	–	5.501	[8]
Zr_2Al	$Co_{1.75}Ge$	*hP*6	$P6_3/mmc$	4.882	–	5.918	[9]
ht-Zr_5Al_3	W_5Si_3	*tI*32	*I*4/*mcm*	11.049	–	5.396	[10]
stab-Zr_5Al_3	Mn_5Si_3	*hP*16	$P6_3/mcm$	8.184	–	5.702	[11]
Zr_3Al_2	Zr_3Al_2	*tP*20	$P4_2/mnm$	7.630	–	6.998	[12]
Zr_4Al_3	Zr_4Al_3	*hP*7	*P*6/*mmm*	5.433	–	5.390	[13]
ht-Zr_5Al_4	Ti_5Ga_4	*hP*18	$P6_3/mcm$	8.447	–	5.810	[14]
ZrAl	TlI	*oS*8	*Cmcm*	3.353	10.866	4.266	[15]
Zr_2Al_3	Zr_2Al_3	*oF*40	*Fdd*2	5.572	9.598	13.879	[9]
$ZrAl_2$	$MgZn_2$	*hP*12	$P6_3/mmc$	5.2824	–	8.7482	[16]
$ZrAl_3$	$ZrAl_3$	*tI*16	*I*4/*mmm*	4.00930	–	17.2718	[17]
$Zr_{3.2}Sn_{0.8}$	Cr_3Si	*cP*8	*Pm*-3*n*	5.625	–	–	[18]
Zr_5Sn_3	Mn_5Si_3	*hP*16	$P6_3/mcm$	8.4576	–	5.7797	[19]
Zr_5Sn_4	Ti_5Ga_4	*hP*18	$P6_3/mcm$	8.759	–	5.916	[20]
$ZrSn_2$	$TiSi_2$	*oF*24	*Fddd*	9.573	5.644	9.927	[21]

Experimental

15 two-component and 44 three-component alloys were synthesized by arc melting from high-purity metals (Zr ≥ 99.9 wt.%, Al ≥ 99.99 wt.%, Sn ≥ 99.99 wt.%), using a tungsten electrode and a water-cooled copper hearth under a Ti-gettered argon atmosphere. To achieve homogeneity the samples were melted twice. The synthesized alloys, wrapped into tantalum foil, were homogenized in sealed quartz ampoules under vacuum at 600°C for 720 h. Finally, the ampoules containing the samples were quenched into cold water. The weight losses, which were controlled at all stages of the synthesis, did not exceed 0.5 % of the total mass, which was approximately 1 g for each alloy.

Phase analysis and structure refinements were performed using X-ray powder diffraction data collected at room temperature on diffractometers DRON-2.0M (Fe *K*α-radiation, angular range $10\text{-}20° \leq 2\theta \leq 120\text{-}140°$, step 0.05°) and STOE Stadi P (Cu $K\alpha_1$-radiation, angular range $6° \leq 2\theta \leq 110°$, step 0.015°). The profile and structural parameters were refined by the Rietveld method, using the program package FullProf Suite [22]. The backgrounds were defined by polynomial functions using the Fourier filtering technique. The phase equilibria and the compositions of the individual phases were additionally analyzed by energy-dispersive X-ray spectroscopy (EDX), performed on a scanning electron microscope TESCAN Vega3 LMU equipped with an energy dispersion X-ray analyzer Oxford Instruments Aztec ONE with a detector X-Max^{N}20.

Results and Discussion

Binary systems

By comparing the experimental X-ray powder diffraction patterns of the two-component alloys with patterns calculated for the known binary compounds, the existence and crystal structures of 12 binaries in the systems Zr–Al and Zr–Sn at 600°C was confirmed: Zr_3Al, Zr_2Al (structure type $Co_{1.75}Ge$), Zr_3Al_2, Zr_4Al_3, ZrAl, Zr_2Al_3, $ZrAl_2$, $ZrAl_3$, $Zr_{3.2}Sn_{0.8}$, Zr_5Sn_3, Zr_5Sn_4, and $ZrSn_2$. The binary aluminides *ht*-Zr_5Al_3, *ht*-Zr_5Al_4, and *stab*-Zr_5Al_3, reported in the literature, were not observed at 600°C. The results obtained here are in good agreement with the phase diagrams of the corresponding binary systems evaluated in [4,5].

Isothermal section of the phase diagram of the system Zr–Al–Sn at 600°C

The isothermal section of the phase diagram of the ternary system Zr–Al–Sn at 600ºC was constructed in the whole concentration range (Fig. 1). It consists of 18 single-phase, 36 two-phase, and 19 three-phase fields. The solid solution based on the binary compound Zr_5Al_4 and the ternary compound $Zr_5Al_{1.68\text{-}0.40}Sn_{1.32\text{-}2.60}$ form the largest number of equilibria (8). At 600°C, Sn and the alloys of the binary system Al–Sn (up to 80 at.% Al) are liquid. The boundary of the liquid phase in the ternary system was extrapolated from its limits in the binary systems: 3.5 at.% Zr in the system Zr–Sn and 80 at.% Al in the system Al–Sn. Three phases, Al, $ZrSn_2$, and $ZrAl_{2.68}Sn_{0.32}$, are in equilibrium with the liquid phase.

The binary compounds Zr_5Sn_4 (structure type Ti_5Ga_4) and Zr_5Sn_3 (structure type Mn_5Si_3) dissolve 11.1 and 2.5 at.% Al, respectively, forming solid

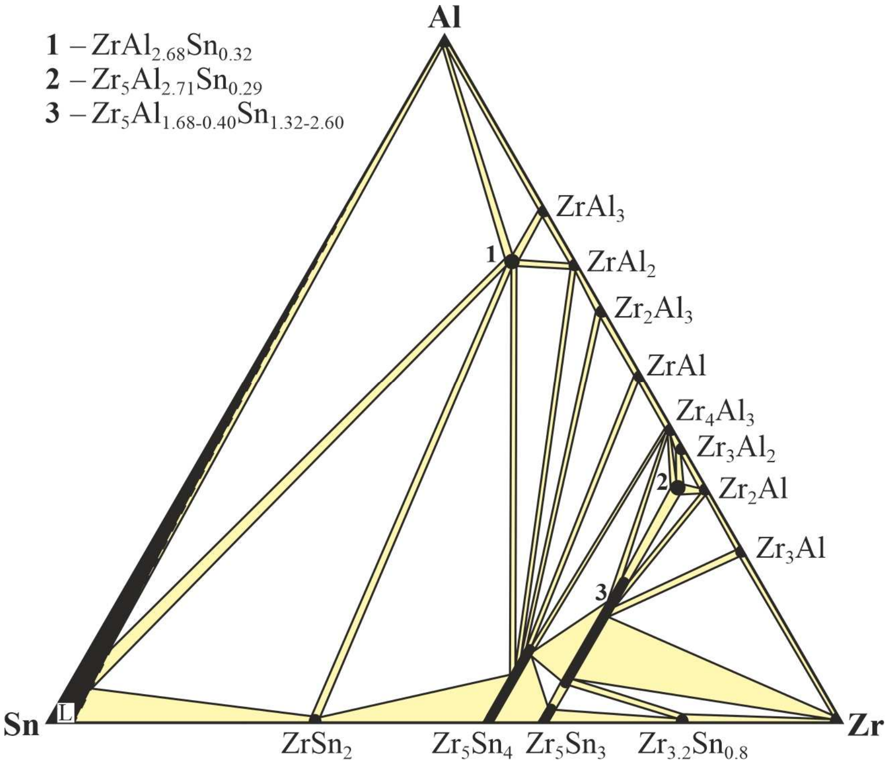

Fig. 1 Isothermal section of the phase diagram of the ternary system Zr–Al–Sn at 600°C.

Table 2 Atomic coordinates and isotropic displacement parameters for Zr_5AlSn_3 (structure type Hf_5CuSn_3, *hP*18, *P*6_3/*mcm*, a = 8.6184(19), c = 5.8656(14) Å, R_B = 0.0680).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Zr1	6*g*	0.2610(7)	0	¼	0.73(8)
Zr2	4*d*	⅓	⅔	0	0.78(8)
Al	2*b*	0	0	0	1.12(11)
Sn	6*g*	0.6128(7)	0	¼	0.89(9)

solutions of the substitution type, characterized by a constant Zr content. The solubilities of the third component in the other binary compounds of the systems Zr–Al and Zr–Sn do not exceed 1 at.%. Three ternary compounds exist in the system Zr–Al–Sn at 600°C. The compounds $ZrAl_{2.68}Sn_{0.32}$ and $Zr_5Al_{2.71}Sn_{0.29}$ have point compositions, whereas the compound $Zr_5Al_{1.68-0.40}Sn_{1.32-2.60}$ exhibits a homogeneity range of 16 at.% Al (Sn) at a constant Zr content of 62.5 at.%.

By means of EDX and X-ray diffraction it was established that the composition Zr_5AlSn_3, reported in [3], corresponds to the boundary composition of the solid solution of the substitution type based on the binary compound Zr_5Sn_4. The crystal structure of Zr_5AlSn_3 was determined by a Rietveld refinement carried out using a diffraction pattern collected on the DRON-2.0M diffractometer (Table 2). It belongs to the structure type Hf_5CuSn_3 (*hP*18, *P*6_3/*mcm*, a = 8.6184(19), c = 5.8656(14) Å) which is a ternary variant of the structure type Ti_5Ga_4 and is characterized by ordering of the Al and Sn atoms in two crystallographic sites: the position 2*b* is occupied by Al atoms, while the position 6*g* is occupied by Sn atoms. The structure types Ti_5Ga_4 and Hf_5CuSn_3 are, respectively, binary and ternary filled variants of the structure type Mn_5Si_3, to which the structure of the binary aluminide Zr_5Sn_3 belongs. However, direct inclusion of Al atoms into the structure of Zr_5Sn_3, *i.e.* the formation of an inclusion solid solution based on Zr_5Sn_3, was not observed in the ternary system at 600°C. Ternary phases with Hf_5CuSn_3-type structures have also been reported for related systems with Zr and Hf. Zr_5AlGe_3 [23] and Hf_5GaSb_3 [24] are ternary compounds, whereas Hf_5GaSn_3 is the limiting composition of the inclusion-type solid solution $Hf_5Ga_xSn_3$ (x = 0-1) [25,26]. For two phases, Zr_5AlSb_3 [27] and Zr_5GaSn_3 [3] the way of formation is not known.

The Al atoms in the structure of Zr_5AlSn_3 occupy the position at the origin of the unit cell, centering Zr_6 octahedra that are connected by common faces and form 1D-rods along the crystallographic direction [001]. These rods of $AlZr_6$ octahedra occupy tunnels formed by $ZrSn_6$ octahedra connected via common edges in the plane (001), as described for Zr_5AlGe_3 in [23].

Crystal structures of the ternary compounds

Substitution of Sn atoms for Al atoms in $ZrAl_3$ led to the formation of the ternary compound $ZrAl_{2.68}Sn_{0.32}$. The constant values of the cell parameters, and of the composition determined by EDX analysis of different multiphase samples, allowed us to conclude on the absence of significant solubility of Sn in the binary aluminide $ZrAl_3$ and on a point composition for the ternary compound. The crystal structure of the ternary compound $ZrAl_{2.68}Sn_{0.32}$ was refined by the Rietveld method, using the X-ray powder diffraction pattern of a single-phase alloy of nominal composition $Zr_{25}Al_{67}Sn_8$, collected on the powder diffractometer STOE Stadi P (Fig. 2). Experimental details and crystallographic data for $ZrAl_{2.68}Sn_{0.32}$ are listed in Table 3.

The partially disordered structure of the ternary compound with refined composition $ZrAl_{2.682(4)}Sn_{0.318(4)}$ belongs to the tetragonal structure type *ht*-$TiAl_3$. Atom coordinates and isotropic displacement parameters are given in Table 4. The structure has one site in Wyckoff position 2*a* occupied by Zr atoms, one site (2*b*) by Al atoms, and one site (4*d*) by a statistical mixture of Al and Sn atoms. Complete ordering of the Al and Sn atoms on the two latter sites would lead to the composition $ZrAl_2Sn$ and a structure of the $UCuAl_2$-type, which is a ternary ordered variant of the structure type *ht*-$TiAl_3$. The composition of the ternary compound determined by EDX analysis ($Zr_{1.00(2)}Al_{2.68(2)}Sn_{0.32(2)}$) is in good agreement with the composition obtained from the Rietveld refinement.

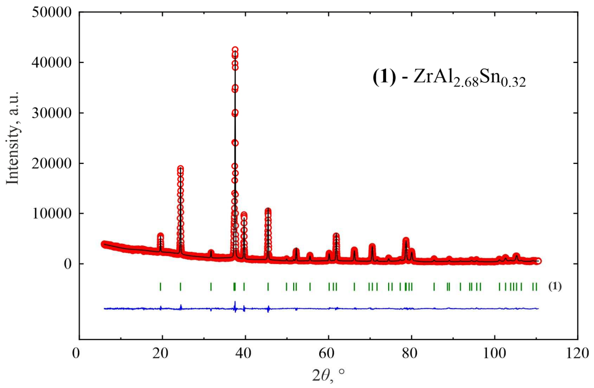

Fig. 2 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the sample $Zr_{25}Al_{67}Sn_8$ (radiation Cu $K\alpha_1$). Vertical bars indicate the positions of the reflections for $ZrAl_{2.68}Sn_{0.32}$.

Table 3 Experimental details and crystallographic data for $ZrAl_{2.68}Sn_{0.32}$ (in the sample $Zr_{25}Al_{67}Sn_8$).

Refined composition	$ZrAl_{2.682(4)}Sn_{0.318(4)}$
Structure type	*ht*-$TiAl_3$
Pearson symbol	*tI*8
Space group	*I*4/*mmm*
Cell parameters *a*, *c*, Å	3.98855(18), 9.0848(4)
Cell volume *V*, $Å^3$	144.526(12)
Formula units per cell *Z*	2
Density D_X, g cm^{-3}	4.426
Preferred orientation: value / [direction]	0.981(4) / [110]
Reliability factor R_B	0.0380
Profile parameters *U*, *V*, *W*	0.116(7), 0.018(6), 0.0227(13)
Shape parameter	0.343(7)
Asymmetry parameters	0.064(5), 0.0174(16)
Reliability factors R_p, R_{wp}, χ^2	0.0327, 0.0461, 1.53

Table 4 Atomic coordinates, site occupancies and isotropic displacement parameters for $ZrAl_{2.682(4)}Sn_{0.318(4)}$ (structure type $TiAl_3$, *tI*8, *I*4/*mmm*, *a* = 3.98855(18), *c* = 9.0848(4) Å).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, $Å^2$
Zr	2*a*	0	0	0	0.69(5)
Al	2*b*	0	0	½	1.27(14)
M (0.841(2)Al+0.159(2)Sn)	4*d*	0	½	¼	1.23(8)

The tetragonal structure types *ht*-$TiAl_3$, $UCuAl_2$, and $ZrAl_3$ derive from the cubic structure type Cu and belong to the family of cubic close-packed structures. All three structures are built from close-packed layers, which are stacked along the crystallographic direction [001] of the tetragonal unit cell. The coordination polyhedra of the atoms in these structures are cuboctahedra. Isotypic representatives of the structure type *ht*-$TiAl_3$ ($ZrAl_{2.52}Ge_{0.48}$ and $HfAl_{2.40}Ge_{0.60}$) exist at 600°C in the related systems {Zr,Hf}–Al–Ge [17].

Two ternary compounds exist in the Zr-rich region (on the line with 62.5 at.% of Zr) of the system Zr–Al–Sn at 600°C. The new ternary compound $Zr_5Al_{2.71}Sn_{0.29}$ has a point composition, whereas the compound $Zr_5Al_{1.68\text{-}0.40}Sn_{1.32\text{-}2.60}$, reported in [4] at the composition Zr_5AlSn_2, has a homogeneity region of 16 at.% of Al(Sn). The crystal structures were determined by X-ray powder diffraction from experimental patterns collected at room temperature (diffractometer STOE Stadi P) from the samples $Zr_{62.5}Al_{32.5}Sn_5$ and $Zr_{62.5}Al_5Sn_{32.5}$ (Fig. 3).

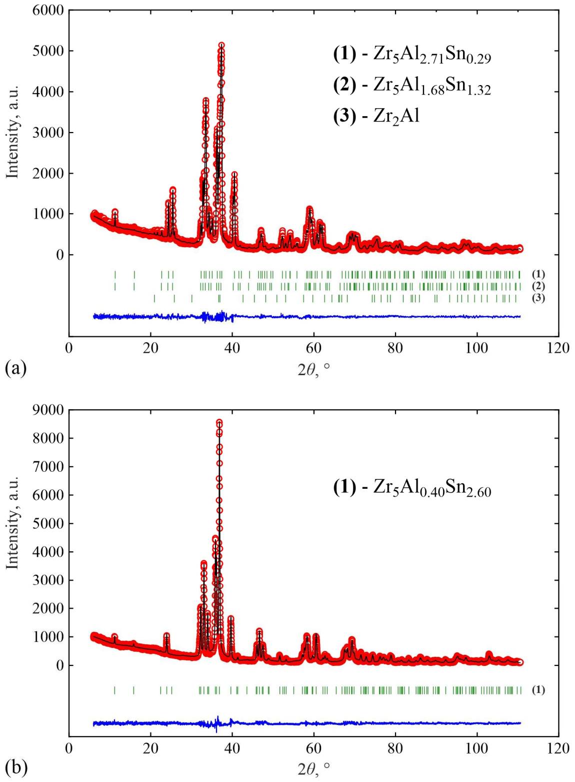

Fig. 3 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the samples (a) $Zr_{62.5}Al_{32.5}Sn_5$ and (b) $Zr_{62.5}Al_5Sn_{32.5}$ (radiation Cu $K\alpha_1$). Vertical bars indicate the positions of reflections of the individual phases.

The sample $Zr_{62.5}Al_{32.5}Sn_5$ contained three phases: ternary phases $Zr_5Al_{2.71}Sn_{0.29}$ and $Zr_5Al_{1.68}Sn_{1.32}$ (Al-rich border of the homogeneity region of $Zr_5Al_{1.68\text{-}0.40}Sn_{1.32\text{-}2.60}$) with W_5Si_3-type structures, and the $Co_{1.75}Ge$-type binary aluminide Zr_2Al. The sample $Zr_{62.5}Al_5Sn_{32.5}$ contained a single ternary phase, $Zr_5Al_{0.40}Sn_{2.60}$ (Sn-rich border of the homogeneity region). Thus, crystallographic parameters for the ternary compound of variable composition were refined at the limiting compositions of its homogeneity range. Experimental details and crystallographic data for the ternary phases in the samples $Zr_{62.5}Al_{32.5}Sn_5$ and $Zr_{62.5}Al_5Sn_{32.5}$ are listed in Table 5. The compositions determined by EDX analysis ($Zr_{5.01(4)}Al_{2.69(5)}Sn_{0.31(6)}$, $Zr_{5.04(4)}Al_{1.66(6)}Sn_{1.37(6)}$, and $Zr_{4.97(8)}Al_{0.43(7)}Sn_{2.60(9)}$) agree with the compositions obtained from the Rietveld refinements.

The crystal structures of the ternary compounds $Zr_5Al_{2.71}Sn_{0.29}$ and $Zr_5Al_{1.68\text{-}0.40}Sn_{1.32\text{-}2.60}$ belong to the tetragonal structure type W_5Si_3, which contains four atom sites (Table 6). In both phases the sites in Wyckoff positions 16*k* and 4*b* are occupied by Zr atoms, whereas the occupation of the positions 8*h* and 4*a* by Al or Sn atoms depends on the composition of the phase. In the structure of the Al-rich ternary compound with point composition $Zr_5Al_{2.71}Sn_{0.29}$ the site in Wyckoff position 8*h* is occupied by a statistical mixture of Al and Sn atoms, whereas position 4*a* is exclusively occupied by Al atoms. A similar, partially disordered distribution of the atoms was also observed in the structure of the related ternary compound $Zr_5Al_{2.70}Ge_{0.30}$ [28]. The distribution of the *p*-element atoms in the structure of the ternary compound of variable composition $Zr_5Al_{1.68\text{-}0.40}Sn_{1.32\text{-}2.60}$ changes with the Al(Sn) content. Near the Al-rich border, positions 8*h* and 4*a* are both occupied by statistical mixtures of Al and Sn atoms, whereas at the Sn-rich border the position 8*h* is exclusively occupied by Sn atoms and the position 4*a* by a mixture of Al and Sn atoms. Complete ordering of the Al and Sn atoms would lead to the structure type Nb_5SiSn_2 (*tI*32, *I*4/*mcm*), which is a ternary variant of the structure type W_5Si_3, at the compositions Zr_5Al_2Sn (Al atoms in the position 8*h*, Sn atoms in 4*a*) or Zr_5AlSn_2 (Sn atoms in 8*h*, Al atoms in 4*a*). The composition Zr_5Al_2Sn is located in the two-phase region between the two ternary compounds, whereas Zr_5AlSn_2 is included in the homogeneity range of the ternary compound $Zr_5Al_{1.68\text{-}0.40}Sn_{1.32\text{-}2.60}$.

The polyhedra around the atoms in the structures of the ternary compounds $Zr_5Al_{2.71}Sn_{0.29}$ and $Zr_5Al_{1.68\text{-}0.40}Sn_{1.32\text{-}2.60}$ are typical for W_5Si_3 (Nb_5SiSn_2)-type compounds: 15- and 14-vertex Frank-Kasper polyhedra around the sites Zr1 and Zr2, respectively, defect icosahedra around the *p*-element (*M*) atoms in the position 8*h*, and square antiprisms with two additional atoms around the *p*-element atoms in the position 4*a*. The structures are built up from infinite columns of *M*-centered square antiprisms Zr_8 (*M* in position 4*a*) and Zr-centered tetrahedra M_4 (*M* in position 8*h*) along the crystallographic direction [001], as described for $Zr_5Al_{2.70}Ge_{0.30}$ in [28]. The ternary W_5Si_3-type phases, $Zr_5Al_{2.71}Sn_{0.29}$ and $Zr_5Al_{1.68\text{-}0.40}Sn_{1.32\text{-}2.60}$, are individual ternary compounds at 600°C, however the Al-rich phase $Zr_5Al_{2.71}Sn_{0.29}$ may correspond to the high-temperature phase *ht*-Zr_5Al_3, which exists at higher above 1000°C, stabilized by Sn atoms at lower temperatures.

Ternary compounds with W_5Si_3-type (Nb_5SiSn_2-type) structures have also been reported in the related systems Hf–{Al,Ga}–{Sn,Sb} [4,25,29,30].

Table 5 Experimental details and crystallographic data for the individual phases in the samples $Zr_{62.5}Al_{32.5}Sn_5$ and $Zr_{62.5}Al_5Sn_{32.5}$.

Sample		$Zr_{62.5}Al_{32.5}Sn_5$			$Zr_{62.5}Al_5Sn_{32.5}$
Refined composition		$Zr_5Al_{2.71(1)}Sn_{0.29(1)}$	$Zr_5Al_{1.68(3)}Sn_{1.32(3)}$	Zr_2Al	$Zr_5Al_{0.40(1)}Sn_{2.60(1)}$
Content, mass %		54.4(5)	38.5(6)	7.1(1)	100
Structure type		W_5Si_3	W_5Si_3	$Co_{1.75}Ge$	W_5Si_3
Pearson symbol		*tI*32	*tI*32	*hP*6	*tI*32
Space group		*I*4/*mcm*	*I*4/*mcm*	$P6_3/mmc$	*I*4/*mcm*
Cell parameters	*a*, Å	11.0530(9)	11.1005(9)	4.8842(8)	11.1829(12)
	c, Å	5.4071(5)	5.4537(5)	5.9186(10)	5.5449(6)
Cell volume *V*, Å^3		660.58(10)	672.01(10)	330.23(11)	693.43(13)
Formula units per cell *Z*		4	4	2	4
Density D_X, g cm^{-3}		5.670	6.503	5.656	7.257
Preferred orientation: value / [direction]		0.933(3) / [001]	0.888(4) / [110]	–	0.971(3) / [110]
Reliability factor	R_B	0,0500	0,0362	–	0.0581
Profile parameters	*U*	0.253(17)			0.075(19)
	V	0.055(14)			0.107(18)
	W	0.007(3)			0.008(3)
Shape parameter		0.727(10)			0.742(11)
Asymmetry parameters	P_1	0.056(10)			0.022(8)
	P_2	0.008(3)			0.0037(18)
Reliability factors	R_p	0.0314			0.0366
	R_{wp}	0.0416			0.0421
	χ^2	1.53			1.62

Table 6 Atomic coordinates, site occupancies, and isotropic displacement parameters for the ternary compounds $Zr_5Al_{2.71}Sn_{0.29}$ and $Zr_5Al_{1.68\text{-}0.40}Sn_{1.32\text{-}2.60}$ (structure type W_5Si_3, *tI*32, *I*4/*mcm*).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
$Zr_5Al_{2.71(1)}Sn_{0.29(1)}$					
Zr1	16*k*	0.08003(17)	0.21966(16)	0	0.59(5)
Zr2	4*b*	0	½	¼	0.61(9)
0.854(5)Al + 0.146(5)Sn	8*h*	0.1666(4)	0.6666(4)	¼	1.1(2)
Al	4*a*	0	0	¼	0.9(3)
$Zr_5Al_{1.68(3)}Sn_{1.32(3)}$					
Zr1	16*k*	0.0792(2)	0.2172(3)	0	0.63(7)
Zr2	4*b*	0	½	¼	0.45(12)
0.427(16)Al + 0.573(16)Sn	8*h*	0.1643(3)	0.6643(3)	¼	1.4(2)
0.827(15)Al + 0.173(15)Sn	4*a*	0	0	¼	1.5(3)
$Zr_5Al_{0.40(1)}Sn_{2.60(1)}$					
Zr1	16*k*	0.07826(19)	0.21869(18)	0	0.31(4)
Zr2	4*b*	0	½	¼	0.54(9)
Sn	8*h*	0.16467(14)	0.66467(14)	¼	1.03(6)
0.596(10)Al + 0.404(10)Sn	4*a*	0	0	¼	1.1(2)

Conclusions

The ternary system Zr–Al–Sn at 600°C is characterized by the existence of limited solid solutions based on the binary compounds Zr_5Sn_4 (11.1 at.% Al) and Zr_5Sn_3 (2.5 at.% Al), and three ternary compounds, $ZrAl_{2.68}Sn_{0.32}$ (structure type $TiAl_3$), $Zr_5Al_{2.71}Sn_{0.29}$ and $Zr_5Al_{1.68\text{-}0.40}Sn_{1.32\text{-}2.60}$ (both with structure type W_5Si_3). The ternary phases show partial ordering of Al and Sn atoms. The structure type $TiAl_3$ ($ZrAl_{2.68}Sn_{0.32}$) is a member of the family of cubic close-packed structures and is consequently built up by cuboctahedra. The structures of the phases with high Zr-content are built up from columns of octahedra (in Zr_5AlSn_3, boundary composition of the solid solution $Zr_5Al_xSn_{4-x}$), or square antiprisms and tetrahedra in the isotypic compounds $Zr_5Al_{2.71}Sn_{0.29}$ and $Zr_5Al_{1.68\text{-}0.40}Sn_{1.32\text{-}2.60}$.

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