Chemistry of Metals and Alloys

Chem. Met. Alloys 16 (2023) 26-31
Ivan Franko National University of Lviv
http://publications.lnu.edu.ua/chemetal

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

Danylo MARYSKEVYCH[1]*, Yaroslav TOKAYCHUK[1], Roman GLADYSHEVSKII[1]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv,*
Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
* *Corresponding author. E-mail: danylo.maryskevych@lnu.edu.ua*

Received March 24, 2023; accepted June 29, 2023
https://doi.org/10.30970/cma16.0436

The isothermal section at 600°C of the phase diagram of the ternary system Hf–Al–Sn was constructed in the whole concentration range, using X-ray powder diffraction and energy-dispersive X-ray spectroscopy. A limited solid solution of inclusion type (up to 11.1 at.% Al), based on the binary compound Hf_5Sn_3, forms in the system. The crystal structure of Hf_5AlSn_3 (boundary composition of the solid solution $Hf_5Al_xSn_3$) belongs to the structure type Hf_5CuSn_3 (Pearson symbol *hP*18, space group $P6_3/mcm$, a = 8.5594(15), c = 5.7996(12) Å, Z = 2), which is a ternary filled-up variant of the structure type Mn_5Si_3, to which the structure of the binary compound Hf_5Sn_3 belongs. Three ternary compounds exist at 600°C: $HfAl_{2.636(2)}Sn_{0.364(2)}$ (structure type ht-$TiAl_3$, *tI*8, $I4/mmm$, a = 3.95575(10), c = 8.9473(2) Å, Z = 2), $Hf_5Al_{2.70(4)}Sn_{0.30(4)}$ (Mn_5Si_3, *hP*16, $P6_3/mcm$, a = 8.0910(6), c = 5.6515(4) Å, Z = 2), and $Hf_5Al_{1.33(3)\text{-}0.782(10)}Sn_{1.67(2)\text{-}2.218(10)}$ (Nb_5SiSn_2, *tI*32, $I4/mcm$, a = 10.9331(9)-11.0348(6), c = 5.5012(5)-5.5611(3) Å, Z = 4). The structure of $HfAl_{2.64}Sn_{0.36}$ is derived from the cubic close-packed structure and the coordination polyhedra are cuboctahedra.

Hafnium / Aluminum / Tin / X-ray powder diffraction / Phase diagram / Solid solution / Ternary compound / Crystal structure

Introduction

The phase diagram of the ternary system Hf–Al–Sn has so far not been investigated. The formation of one ternary compound has been reported [1]: Hf_5AlSn_2 (structure type Nb_5SiSn_2, Pearson symbol *tI*32, space group $I4/mcm$) [2]. The unit-cell parameters were determined (a = 11.014, c = 5.542 Å), and the structure type was assigned, but the positional and occupancy parameters or the homogeneity range were not determined. Among related ternary systems, isothermal sections of the phase diagrams have been constructed for the systems Ti–Al–Sn (at 900°C in the region 33.3-100 at.% Ti) [3], Zr–Al–Sn (at 600°C) [4], and Hf–Ga–Sn (at 600°C) [5]. Crystallographic data for the ternary compounds that form in the ternary systems {Ti,Zr}–Al–Sn and Hf–Ga–Sn are summarized in Table 1. Common features for these systems are the formation of solid solutions based on the binary compounds, mainly in the transition metal-rich part of the system, and the existence of ternary compounds with Nb_5SiSn_2-type structure. Limited solid solutions based on the Mn_5Si_3-type (*hP*16, $P6_3/mcm$) binary stannides Ti_5Sn_3, Zr_5Sn_3, and Hf_5Sn_3 form by different mechanisms: *via* partial substitution of Al atoms for Sn atoms in the Zr–Al–Sn system, or *via* inclusion of additional Al or Ga atoms in the systems Ti–Al–Sn and Hf–Ga–Sn. In the system Hf–Ga–Sn the inclusion-type solid solution $Hf_5Ga_xSn_3$ extends to the composition Hf_5GaSn_3 [5,7], which is characterized by an ordered Hf_5CuSn_3-type atom arrangement (*hP*18, $P6_3/mcm$).

The binary systems that delimit the ternary system Hf–Ga–Sn are known in the whole concentration range and the corresponding phase diagrams have been constructed [8,9]. Seven binary gallides were found in the system Hf–Ga. The formation and crystal structures of eight binary aluminides have been reported in the Hf–Al system and of four binary stannides in the system Hf–Sn [1]. Crystallographic data for the binary compounds formed in the systems Hf–Al and Hf–Sn are given in Table 2. The system Ga–Sn is characterized by a eutectic reaction at 228°C and 97.4 at.% Sn and the absence of binary compounds. At 600°C (temperature used in the present investigation) tin is liquid, *i.e.* a liquid region will exist in the Sn-rich corner of the isothermal section of the phase diagram of the system Hf–Al–Sn.

Table 1 Crystallographic data for ternary compounds reported in the systems {Ti,Zr}–Al–Sn and Hf–Ga–Sn.

Compound	Structure type	Pearson symbol	Space group	Cell parameters, Å		Reference
				a	*c*	
Ti_5AlSn_2	Nb_5SiSn_2	*tI*32	*I*4/*mcm*	10.558	5.262	[6]
$ZrAl_{2.68}Sn_{0.32}$	$TiAl_3$	*tI*8	*I*4/*mmm*	3.98855	9.0848	[4]
$Zr_5Al_{2.71}Sn_{0.29}$	W_5Si_3	*tI*32	*I*4/*mcm*	11.0530	5.4071	[4]
$Zr_5Al_{1.68-0.40}Sn_{1.32-2.60}$	W_5Si_3 (Nb_5SiSn_2)	*tI*32	*I*4/*mcm*	11.1005-11.1829	5.4537-5.5449	[4]
$Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$	Nb_5SiSn_2	*tI*32	*I*4/*mcm*	10.9154-11.0203	5.51311-5.56591	[5]

Table 2 Crystallographic data for binary compounds reported in the systems Hf–Al and Hf–Sn.

Compound	Structure type	Pearson symbol	Space group	Cell parameters, Å			Reference
				a	*b*	*c*	
Hf_2Al	$CuAl_2$	*tI*12	*I*4/*mcm*	6.776	–	5.372	[10]
stab-Hf_5Al_3	Mn_5Si_3	*hP*16	$P6_3/mcm$	8.052	–	5.690	[11]
Hf_3Al_2	Zr_3Al_2	*tP*20	$P4_2/mnm$	7.535	–	6.906	[12]
Hf_4Al_3	Zr_4Al_3	*hP*7	*P*6/*mmm*	5.343	–	5.422	[13]
HfAl	TlI	*oS*8	*Cmcm*	3.253	10.831	4.282	[14]
Hf_2Al_3	Zr_2Al_3	*oF*40	*Fdd*2	9.529	13.763	5.522	[15]
$HfAl_2$	$MgZn_2$	*hP*12	$P6_3/mmc$	5.288	–	8.739	[16]
ht-$HfAl_3$	ht-$TiAl_3$	*tI*8	*I*4/*mmm*	3.893	–	8.925	[13]
rt-$HfAl_3$	$ZrAl_3$	*tI*16	*I*4/*mmm*	3.9849	–	17.1443	[17]
$HfSn_2$	$CrSi_2$	*hP*9	$P6_222$	5.4816	–	7.6113	[5]
HfSn	FeSi	*cP*8	$P2_13$	5.594	–	–	[18]
Hf_5Sn_4	Ti_5Ga_4	*hP*18	$P6_3/mcm$	8.740	–	5.910	[19]
Hf_5Sn_3	Mn_5Si_3	*hP*16	$P6_3/mcm$	8.36562	–	5.70775	[5]

This work presents the results of an experimental investigation of the phase equilibria in the ternary system Hf–Al–Sn at 600°C in the whole concentration range. The crystallographic parameters for Hf_5AlSn_3, which corresponds to the limiting composition of the inclusion-type solid solution $Hf_5Al_xSn_3$ (x = 0-1) and for three new ternary compounds, have been derived from X-ray powder diffraction.

Experimental

12 two-component and 42 three-component alloys were synthesized by arc melting from high-purity metals (Hf ≥ 99.95 mass%, Al ≥ 99.99 mass%, Sn ≥ 99.99 mass%), using a water-cooled copper hearth and a tungsten electrode under an argon atmosphere, purified by using Ti sponges as a getter. To achieve homogeneity, the samples were melted twice. The resulting alloys were wrapped into tantalum foil to ensure their isolation, sealed in quartz ampoules under vacuum, and annealed at 600°C for 720 h. Finally, the ampoules with the samples were quenched into cold water. The weight losses, which were controlled at all stages of the synthesis, did not exceed 1 mass%.

Phase analysis and structure refinements were performed using X-ray powder diffraction data collected at room temperature on diffractometers DRON-2.0M (Fe $K\alpha$-radiation, angular range $20° \leq 2\theta \leq 120\text{-}140°$, 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 [20]. For the ternary phases, atomic coordinates reported for the structure types or for related phases were chosen as starting models for the refinement. Backgrounds were defined by a polynomial function using the Fourier filtering technique. The phase equilibria and the compositions of the individual phases were analyzed by energy-dispersive X-ray spectroscopy (EDX), performed on a scanning electron microscope TESCAN Vega3 LMU equipped with an energy-dispersive X-ray analyzer Oxford Instruments Aztec ONE with a detector X-Max^{N}20.

Results and discussion

Binary compounds

By means of X-ray diffraction, the existence and crystal structures of 9 binary compounds in the systems Hf–Al and Hf–Sn at 600°C were confirmed: Hf_2Al (structure type $CuAl_2$), Hf_3Al_2 (Zr_3Al_2), Hf_4Al_3 (Zr_4Al_3), HfAl (TlI), Hf_2Al_3 (Zr_2Al_3), $HfAl_2$ ($MgZn_2$), rt-$HfAl_3$ ($ZrAl_3$), Hf_5Sn_3 (Mn_5Si_3), and $HfSn_2$ ($CrSi_2$). The binary aluminide stab-Zr_5Al_3 and the stannides HfSn and Hf_5Sn_4, reported in literature, were not observed under the conditions applied here.

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

The isothermal section of the phase diagram of the ternary system Hf–Al–Sn at 600°C is shown in Fig. 1. It contains 15 single-phase, 30 two-phase, and 16 three-phase fields. The largest number of equilibria (6) form the solid solution $Hf_5Al_xSn_3$ (x = 0-1). 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: 3.0 at.% Hf in the system Hf–Sn and 20 at.% Sn in the system Al–Sn. Three phases, Al, $HfSn_2$, and $HfAl_{2.64}Sn_{0.36}$, are in equilibrium with the liquid phase at 600°C.

The binary compounds dissolve less than 1 at.% of the third component, except Hf_5Sn_3 (structure type Mn_5Si_3), which dissolves 11.1 at.% Al, forming a solid solution of inclusion type. Three ternary compounds exist in the system Hf–Al–Sn at 600°C: $HfAl_{2.64}Sn_{0.36}$ and $Hf_5Al_{2.70}Sn_{0.30}$ have narrow homogeneity ranges, whereas the compound $Hf_5Al_{1.33\text{-}0.78}Sn_{1.67\text{-}2.22}$ has a homogeneity range of 6.9 at.% Al(Sn) at a constant Hf content of 62.5 at.%.

The crystal structure at the limiting composition of the solid solution $Hf_5Al_xSn_3$ (x = 0-1) was refined by the Rietveld method using a diffraction pattern collected on the DRON-2.0M diffractometer. Atom coordinates and isotropic displacement parameters for Hf_5AlSn_3 are listed in Table 3. The structure belongs to the structure type Hf_5CuSn_3 (*hP*18, *P*6₃*/mcm*, a = 8.5594(15), c = 5.7996(12) Å), which represents a ternary filled variant of the structure type Mn_5Si_3, to which the structure of the binary stannide Hf_5Sn_3 belongs.

The Al atoms in the structure of Hf_5AlSn_3 occupy the site at the origin of the unit cell, filling Hf_6 octahedra that are empty in the structure of the binary compound Hf_5Sn_3. The structure is similar to the earlier reported structures of the ternary phases Zr_5AlSn_3 [4] and Hf_5GaSn_3 [7] and can be described as a 3D-framework of $AlHf_6$ and $HfSn_6$ octahedra, in a similar way as already done for Zr_5AlGe_3 [21].

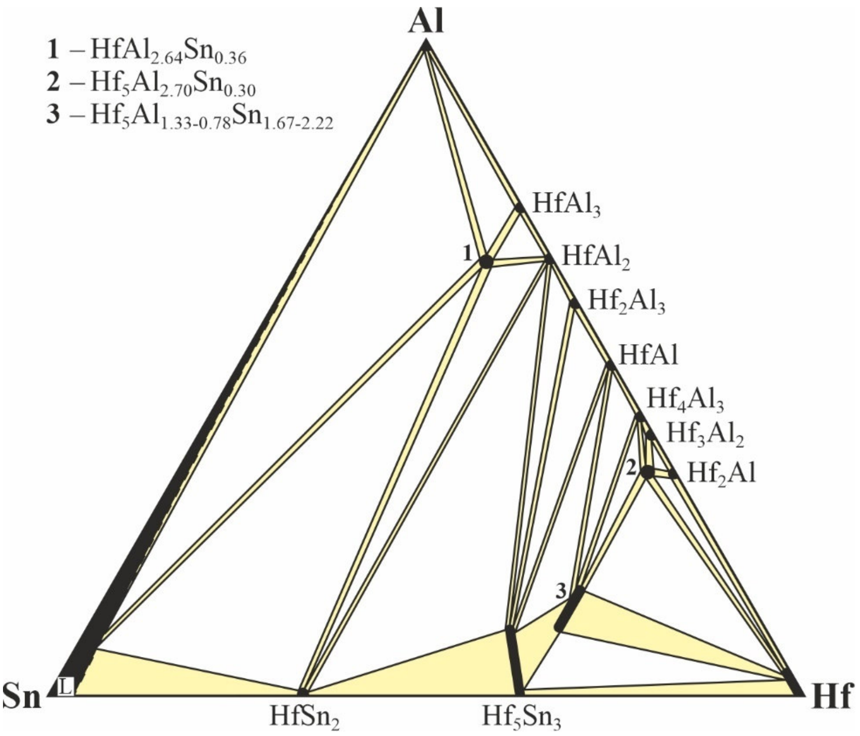

Fig. 1 Isothermal section of the phase diagram of the ternary system Hf–Al–Sn at 600°C.

Table 3 Atom coordinates and isotropic displacement parameters for Hf_5AlSn_3 (Hf_5CuSn_3, *hP*18, *P*6₃*/mcm*, a = 8.5594(15), c = 5.7996(12) Å, R_B = 0.0546).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Hf1	6*g*	0.2706(6)	0	¼	0.42(7)
Hf2	4*d*	⅓	⅔	0	0.51(7)
Al	2*b*	0	0	0	1.02(12)
Sn	6*g*	0.6119(8)	0	¼	0.68(8)

Crystal structures of the ternary compounds

According to the X-ray diffraction phase analysis, substitution of Sn atoms for Al atoms in the $ZrAl_3$-type binary aluminide $HfAl_3$ led to the formation of the ternary compound $HfAl_{2.64}Sn_{0.36}$ with *ht*-$TiAl_3$-type structure. We may assume that the ternary phase $HfAl_{2.64}Sn_{0.36}$, observed at 600°C, is an extension of the high-temperature modification of the binary compound $HfAl_3$, stabilized by Sn atoms at lower temperatures. The crystallographic parameters of the ternary phase were refined by the Rietveld method, using X-ray powder diffraction pattern of a single-phase alloy of nominal composition $Hf_{25}Al_{66}Sn_9$, collected on the powder diffractometer STOE Stadi P (Fig. 2). The atom coordinates in the structure of the related ternary compound $ZrAl_{2.68}Sn_{0.32}$ [4] were used as starting model for the refinement. Experimental details and crystallographic data for $HfAl_{2.64}Sn_{0.36}$ are listed in Table 4. Atom coordinates and isotropic displacement parameters are given in Table 5.

The crystal structure of the ternary compound $HfAl_{2.636(2)}Sn_{0.364(2)}$ belongs to the tetragonal structure type ht-$TiAl_3$ (*tI*8, *I*4/*mmm*, $a = 3.95575(10)$, $c = 8.9473(2)$ Å) and contains three sites in special Wyckoff positions: 2*a* and 2*b* are occupied exclusively by Hf and Al atoms, respectively, and position 4*d* is occupied by a statistical mixture of Al and Sn atoms. Alternative refinements confirmed that the substitution of Sn atoms for Al atoms in the structure of ht-$HfAl_3$ occurs on only one crystallographic site. Similar structural features were observed in the structure of $ZrAl_{2.68}Sn_{0.32}$ [4]. Complete ordering of Al and Sn atoms in the Wyckoff positions 2*b* and 4*d* would lead to the composition $HfAl_2Sn$ and the structure type $UCuAl_2$, which is a ternary ordered variant of the structure type ht-$TiAl_3$.

At 600°C the ternary phase $HfAl_{2.64}Sn_{0.36}$ is a distinct ternary compound forming an equilibrium with the $ZrAl_3$-type binary compound rt-$HfAl_3$. Constant unit-cell parameters in different multiphase samples indicate the absence of significant solubility of Sn in the binary aluminide rt-$HfAl_3$ and a near to point composition for the ternary compound at 600°C. The composition of the latter determined by EDX analysis ($Hf_{1.00(2)}Al_{2.64(2)}Sn_{0.36(2)}$) is in excellent agreement with the composition derived from the Rietveld refinement.

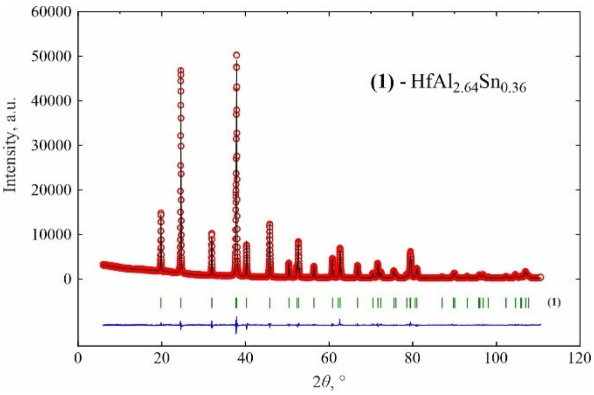

Fig. 2 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the sample $Hf_{25}Al_{66}Sn_9$ (radiation Cu $K\alpha_1$). Vertical bars indicate the positions of reflections for $HfAl_{2.64}Sn_{0.36}$.

Table 4 Experimental details and crystallographic data for $HfAl_{2.64}Sn_{0.36}$.

Refined composition	$HfAl_{2.636(2)}Sn_{0.364(2)}$
Structure type	$TiAl_3$
Pearson symbol	*tI*8
Space group	*I*4/*mmm*
Unit-cell parameters *a*, *c*, Å	3.95575(10), 8.9473(2)
Cell volume *V*, Å^3	140.008(6)
Formula units per cell *Z*	2
Density D_X, g cm^{-3}	6.603
Preferred orientation: value / [direction]	0.903(2) / [110]
Reliability factor R_B	0.0201
Profile parameters *U*, *V*, *W*	0.195(4), -0.034(3), 0.0171(6)
Shape parameter	0.524(4)
Asymmetry parameters	0.059(2), 0.0004(7)
Reliability factors R_p, R_{wp}, χ^2	0.0421, 0.0601, 1.31

Table 5 Atom coordinates, site occupancies and isotropic displacement parameters for $HfAl_{2.636(2)}Sn_{0.364(2)}$ ($TiAl_3$, *tI*8, *I*4/*mmm*, $a = 3.95575(10)$, $c = 8.9473(2)$ Å).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Hf	2*a*	0	0	0	0.601(10)
Al	2*b*	0	0	½	1.17(9)
M (0.818(1)Al+0.182(1)Sn)	4*d*	0	½	¼	0.97(4)

The tetragonal structure types ht-$TiAl_3$, $UCuAl_2$, and $ZrAl_3$ are built from close-packed layers in *c* stacking and are consequently substitution derivatives of the parent f.c.c. type Cu (*cF*4, *Fm*-3*m*). The coordination polyhedra of all the atoms in these structures are cuboctahedra. Ternary compounds with ht-$TiAl_3$-type structure, $ZrAl_{2.52}Ge_{0.48}$ and $HfAl_{2.40}Ge_{0.60}$, also exist in the related systems {Zr,Hf}–Al–Ge [17].

Two ternary compounds exist at 62.5 at.% of Hf in the system Hf–Al–Sn at 600°C: a new ternary compound $Hf_5Al_{2.70}Sn_{0.30}$ with a point composition, and the compound $Hf_5Al_{1.33\text{-}0.78}Sn_{1.67\text{-}2.22}$ with a homogeneity region of 6.9 at.% of Al(Sn), which includes the composition Hf_5AlSn_2 reported in [2]. The crystal structures of these compounds were determined by means of X-ray powder diffraction using experimental patterns (diffractometer DRON-2.0M) collected from the multiphase samples $Hf_{62.5}Al_{34.5}Sn_3$ and $Hf_{62.5}Al_9Sn_{32.5}$.

The sample $Hf_{62.5}Al_{34.5}Sn_3$ contained three phases: the ternary compound $Hf_5Al_{2.70}Sn_{0.30}$ (69 mass%) and the binary aluminides Hf_3Al_2 (17 mass%) and Zr_2Al (14 mass%). The crystal structure of the ternary compound $Hf_5Al_{2.70(4)}Sn_{0.30(4)}$ belongs to the hexagonal structure type Mn_5Si_3, which is characterized by three sites (Table 6). Two sites, in Wyckoff positions 6*g* and 4*d*, are occupied by Hf atoms and the third site (6*g*) by a statistical mixture of Al and Sn atoms. The coordination polyhedra of the atoms in the structure of the ternary compound $Hf_5Al_{2.70}Sn_{0.30}$ are typical for Mn_5Si_3-type phases: 15-vertex polyhedra, which can be described as pentagonal prisms with five additional atoms, for the site Hf1, 14-vertex Frank-Kasper polyhedra for Hf2, and defect icosahedra around the atoms of *p*-block elements. The composition of the ternary phase as determined by EDX analysis ($Hf_{4.99(3)}Al_{2.69(3)}Sn_{0.32(5)}$) agrees with the composition derived from the Rietveld refinement. The compound synthesized here can correspond to the phase stab-Hf_5Al_3 with Mn_5Si_3-type structure, which does not exist in the binary system at 600°C, but can form when stabilized by admixtures.

The sample $Hf_{62.5}Al_9Sn_{32.5}$ contained two phases: the ternary phase $Hf_5Al_{0.78}Sn_{2.22}$, which corresponds to the Sn-rich border of the homogeneity region of $Hf_5Al_{1.33\text{-}0.78}Sn_{1.67\text{-}2.22}$ (89 mass%) and the binary stannide Hf_5Sn_3 (11 mass%). The crystal structure of the ternary phase $Hf_5Al_{0.782(10)}Sn_{2.218(10)}$ belongs to the tetragonal structure type Nb_5SiSn_2 which is a ternary ordered variant of the binary structure type W_5Si_3. The structure is characterized by four crystallographic sites (Table 6): the sites in Wyckoff positions 16*k* and 4*b* are occupied by Hf atoms, position 8*h* by Sn atoms, and position 4*a* by a statistical mixture of Al and Sn atoms.

The polyhedra around the atoms in the structure of this ternary phase are typical for Nb_5SiSn_2-type compounds: 15- and 14-vertex Frank-Kasper polyhedra around sites Hf1 and Hf2, respectively, defect icosahedra around the Sn atoms in the position 8*h*, and square antiprisms with two additional atoms around the *p*-block element atoms in position 4*a*.

The homogeneity range of the tetragonal phase as determined by EDX analysis, $Hf_{5.01(3)}Al_{1.33(3)}Sn_{1.67(2)}$-$Hf_{5.00(3)}Al_{0.78(2)}Sn_{2.22(2)}$, agrees with the results of the X-ray phase analysis and the Rietveld refinements. Within the homogeneity range the unit-cell parameters increase with increasing Sn content: $a = 10.9331(9)\text{-}11.0348(6)$, $c = 5.5012(5)\text{-}5.5611(3)$ Å.

The isothermal section of the phase diagram of the ternary system Hf–Al–Sn at 600°C determined here, shows similar features with the earlier reported related systems {Ti,Zr,Hf}–{Al,Ga}–{Si,Ge,Sn,Sb}. Typical for the systems with Al is the existence of binary and ternary compounds with close-packed structures (structure types ht-$TiAl_3$ and $ZrAl_3$) along the isoconcentrates 25 at.% Hf at high Al content [1]. The existence of a ternary phase with Nb_5SiSn_2-type structure in the system Hf–Al–Sn makes this system similar to the systems {Ti,Zr}–Al–Sn and Hf–Ga–Sn. A peculiarity of the system investigated here is the formation of the inclusion-type solid solution $Hf_5Al_xSn_3$ ($x = 0\text{-}1$).

Table 6 Crystallographic parameters, atom coordinates, site occupancies and isotropic displacement parameters for the ternary compounds $Hf_5Al_{2.70(4)}Sn_{0.30(4)}$ and $Hf_5Al_{0.782(10)}Sn_{2.218(10)}$.

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
$Hf_5Al_{2.70(4)}Sn_{0.30(4)}$ (Mn_5Si_3, *hP*16, *P*6$_3$/*mcm*, $a = 8.0910(6)$, $c = 5.6515(4)$ Å, $Z = 2$, $R_B = 0.0753$)					
Hf1	6*g*	0.2421(5)	0	¼	0.53(6)
Hf2	4*d*	⅓	⅔	0	0.60(6)
M (0.899(13)Al+0.101(13)Sn)	6*g*	0.6148	0	¼	1.1(2)
$Hf_5Al_{0.782(10)}Sn_{2.218(10)}$ (Nb_5SiSn_2, *tI*32, *I*4/*mcm*, $a = 11.0348(6)$, $c = 5.5611(3)$ Å, $Z = 4$, $R_B = 0.0704$)					
Hf1	16*k*	0.0791(4)	0.2226(4)	0	0.55(9)
Hf2	4*b*	0	½	¼	0.58(10)
Sn	8*h*	0.1667(6)	0.6667(6)	¼	0.89(6)
0.782(10)Al + 0.218(10)Sn	4*a*	0	0	¼	0.98(7)

A similar solid solution has been reported for the system Hf–Ga–Sn [5]. Ternary phases with Hf_5CuSn_3-type structure also exist in other related systems with Zr: Zr_5AlGe_3 [21] as a ternary compound and Zr_5AlSn_3 as the boundary composition of a substitution-type solid solution $Zr_5Al_xSn_{4-x}$ [4]. Increasing the Zr or Hf content in the compounds (decrease of the *p*-block element content) changes the coordination environments of the *p*-block element atoms: from cuboctahedral (25 at.% Zr(Hf)) to trigonal-prismatic and octahedral (55.5 at.% Zr(Hf)), and square-antiprismatic and icosahedral (62.5 at.% Zr(Hf)).

Conclusions

The isothermal section of the phase diagram of the ternary system Hf–Al–Sn at 600°C is characterized by the existence of a limited inclusion-type solid solution based on the binary compound Hf_5Sn_3 (up to 11.1 at.% Al) and three ternary compounds, $HfAl_{2.64}Sn_{0.36}$ (structure type $TiAl_3$), $Hf_5Al_{2.70}Sn_{0.30}$ (Mn_5Si_3), and $Hf_5Al_{1.33-0.78}Sn_{1.67-2.22}$ (Nb_5SiSn_2). The structure type $TiAl_3$ ($HfAl_{2.64}Sn_{0.36}$) is a member of the family of cubic close-packed structures.

Acknowledgement

This work was carried out under the grant of the Ministry of Education and Science of Ukraine No. 0121U109766.

References

[1] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park, OH, USA, Release 2022/23.

[2] M.A. Pietzka, J.C. Schuster, *J. Alloys Compd.* 230 (1995) L10-L12. https://doi.org/10.1016/0925-8388(95)02043-8

[3] M.A. Piezka. U. Gruber, J.C. Schuster. *J. Phys. IV, Coll. C7, Suppl. J. Phys. III.* 3 (1993) 473-476.

[4] D. Maryskevych, Ya. Tokaychuk, R. Gladyshevskii, *Chem. Met. Alloys* 15 (2022) 1-7. https://doi.org/10.30970/cma15.0421

[5] I. Voznyak, Ya. Tokaychuk, R. Gladyshevskii, *Chem. Met. Alloys.* 4 (2011) 175-187. https://doi.org/10.30970/cma4.0200

[6] J. Wu, B. Liu, Y. Cui, H. Wang, Z. Wang, Z. Ren, G. Cao, *Supercond. Sci. Technol.* 32 (2019) 045010. https://doi.org/10.1088/1361-6668/ab0453

[7] I. Voznyak, Ya. Tokaychuk, V. Hlukhyy, T.F. Fässler, R. Gladyshevskii, *J. Alloys Compd.* 512 (2012) 246-251. https://doi.org/10.1016/j.jallcom.2011.09.075

[8] T.B. Massalski (Ed.), *Binary Alloy Phase Diagrams*, ASM International, OH, 1990.

[9] P. Villars, H. Okamoto, K. Cenzual (Eds.), *ASM Alloy Phase Diagram Database. Release 2006/2022*, ASM International.

[10] H. Nowotny, O. Schob, F. Benesovsky, *Monatsh. Chem.* 92 (1961) 1300-1303. https://doi.org/10.1007/BF00915000

[11] H. Boller, H. Nowotny, A. Wittmann, *Monatsh. Chem.* 91 (1960) 1174-1184. https://doi.org/10.1007/BF00899845

[12] L.E. Edshammar, *Acta Chem. Scand.* 14 (1960) 1220. https://doi.org/10.3891/acta.chem.scand.14-1219

[13] K. Schubert, T.R. Anantharaman, H.O.K. Ata, H.G. Meissner, M. Pötzschke, W. Rossteutscher, E. Stolz, *Naturwissenschaften* 47 (1960) 512. https://doi.org/10.1007/BF00641115

[14] L.E. Edshammar, *Acta Chem. Scand.* 15 (1961) 403-406. https://doi.org/10.3891/acta.chem.scand.15-0403

[15] L.E. Edshammar, *Acta Chem. Scand.* 14 (1960) 2244. https://doi.org/10.3891/acta.chem.scand.14-2244

[16] L.E. Edshammar, S. Andersson, *Acta Chem. Scand.* 14 (1960) 223-224. https://doi.org/10.3891/acta.chem.scand.14-0223

[17] D. Maryskevych, Ya. Tokaychuk, R. Gladyshevskii, *Solid State Phenom.* 289 (2019) 71-76. https://doi.org/10.4028/www.scientific.net/SSP.289.71

[18] O. Schob, E. Parthé, *Acta Crystallogr.* 17 (1964) 452-453. https://doi.org/10.4028/www.scientific.net/SSP.289.71

[19] K. Schubert, H.G. Meissner, M. Pötzschke, W. Rossteutscher, E. Stolz, Naturwissenschaften 49 (1962) 57. https://doi.org/10.4028/www.scientific.net/SSP.289.71

[20] J. Rodríguez-Carvajal, *Commission on Powder Diffraction (IUCr), Newsletter* 26 (2001) 12-19.

[21] D. Maryskevych, Ya. Tokaychuk, Yu. Prots, L. Akselrud, R. Gladyshevskii, *Chem. Met. Alloys* 12 (2019) 39-43. https://doi.org/10.30970/cma12.039