Chemistry of Metals and Alloys

Chem. Met. Alloys 5 (2012) 84-89
Ivan Franko National University of Lviv
www.chemetal-journal.org

The ternary system Hf–Ga–Si at 600ºC

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Received May 28, 2012; accepted June 27, 2012; available on-line November 5, 2012

The isothermal section of the phase diagram of the ternary system Hf–Ga–Si was constructed in the whole concentration range at 600ºC, using X-ray powder and single-crystal diffraction. Continuous solid solutions $Hf_5Ga_{3-x}Si_x$ (x = 0-3) and $Hf_2Ga_{1-x}Si_x$ (x = 0-1) are formed between the isostructural binary compounds Hf_5Ga_3 and Hf_5Si_3 (structure type Mn_5Si_3) and Hf_2Ga and Hf_2Si (structure type $CuAl_2$). The other binary compounds of the systems Hf–Ga and Hf–Si do not dissolve noticeable amounts of the third component. One ternary compound, $HfGa_{0.33}Si_{0.67}$, is formed in the system (structure type TlI, Pearson symbol *oS*8, space group *Cmcm*, *a* = 3.7338(7), *b* = 9.889(2), *c* = 3.7441(7) Å). No tendency towards ordering of the Ga and Si atoms was observed in the structures of the ternary phases.

Hafnium / Gallium / Silicon / Phase diagram / X-ray diffraction / Crystal structure / Solid solution

Introduction

Among the ternary systems {Ti, Zr, Hf}–{Al, Ga, In}–Si, isothermal sections in the whole concentration regions have been constructed for the systems {Ti, Zr}–Al–Si (at 600 and 1200ºC for both) and {Ti, Zr}–Ga–Si (at 800ºC) [1-4]. Two ternary compounds were found in the system Ti–Al–Si: $Ti_{0.88}Al_{0.24\text{-}0.62}Si_{1.88\text{-}1.50}$ (structure type $Zr_{0.75}AlSi_{1.25}$), $TiAl_{0.30\text{-}0.60}Si_{1.70\text{-}1.40}$ (structure type $ZrSi_2$) and three in the system Zr–Al–Si: $Zr_{0.75}AlSi_{1.25}$ (structure type $Zr_{0.75}AlSi_{1.25}$) [5], $ZrAl_{0.20\text{-}0.25}Si_{0.80\text{-}0.75}$ (structure type TlI) and $ZrAl_{2.70\text{-}2.58}Si_{0.30\text{-}0.42}$ (structure type $TiAl_3$) [6]. The ternary systems {Ti, Zr}–Ga–Si are characterized by the formation of one ternary compound each: $TiGa_{0.20\text{-}0.68}Si_{1.80\text{-}1.32}$ (structure type $ZrSi_2$) and $ZrGa_{0.66\text{-}0.90}Si_{0.34\text{-}0.10}$ (structure type TlI) [4]. Besides, the isothermal section of the phase diagram of the system Ti–Ga–Si at 1350ºC has been constructed in the Ti-rich corner [7-9]. The formation of two ternary compounds, $HfAl_{0.5}Si_{0.5}$ (structure type TlI) [6] and $Hf_{1.95}Al_{0.90}Si_{0.15}$ (structure type $CuAl_2$) [10] was reported for the system Hf–Al–Si. There are no literature data about investigations of ternary silicides of Ti, Zr or Hf with In. Among the ternary systems Hf–Ga–{Si, Ge, Sn} only the system with Sn has been studied in the whole concentration region (at 600ºC) [11]. It is characterized by the formation of one ternary compound, $Hf_5Ga_{1.24\text{-}0.52}Sn_{1.76\text{-}2.48}$ (structure type Nb_5SiSn_2). For the system Hf–Ga–Ge, the existence of a Mn_5Si_3-type continuous solid solution $Hf_5Ga_{3-x}Ge_x$ (x = 0-3) at 600ºC was reported in [12].

The binary systems that delimit the ternary system Hf–Ga–Si have been studied in the whole concentration range and the corresponding phase diagrams constructed [13]. Seven binary gallides were found in the system Hf–Ga. The compounds $Hf_{11}Ga_{10}$ and Hf_5Ga_3 melt congruently at 1700 and 1730ºC, respectively; $HfGa_3$, Hf_2Ga_3, and HfGa form *via* peritectic reactions at 1400, 1480, and 1550ºC, respectively, whereas $HfGa_2$ and Hf_2Ga form *via* peritectoid reactions at 1100 and 1200ºC, respectively. The existence of five binary compounds was reported for the Hf–Si system: Hf_3Si_2 with congruent melting at 2480ºC, and $HfSi_2$, HfSi, Hf_5Si_4, and Hf_2Si, which form peritectically at 1543, 2142, 2320, and 2083ºC, respectively. Additionally, the formation and crystal structure of the binary compound Hf_5Si_3 are reported in the literature [14]. At first this phase was considered to be stabilized by O, N, or C atoms [15-17], however, it was later found to be stable as an individual binary compound [18]. The system Ga–Si is characterized by a eutectic reaction at 99.994 at.% Ga and 29.77ºC. Binary compounds do not form in the Ga–Si system.

In this work we present the results of an investigation of the ternary system Hf–Ga–Si at 600ºC. To the best of our knowledge it is the first time that the interaction of these components is studied. At the temperature of the investigation (600ºC) Ga metal is liquid, thus a liquid region will be observed in the Ga corner.

Experimental

The investigation was carried out on 13 two-component and 75 three-component alloys, which were synthesized from high-purity metals (Hf ≥ 99.9 wt.%, Ga ≥ 99.99 wt.%, Si ≥ 99.999 wt.%) by arc melting, using a tungsten electrode and a water-cooled copper hearth under a Ti-gettered argon atmosphere. To achieve high efficiency of the interaction between the components, the samples were melted twice. After the synthesis the alloys were wrapped into tantalum foil to ensure their isolation, sealed in quartz ampoules under vacuum, and annealed at 600ºC 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 wt.% of the total mass, which was approximately 1 g for each alloy.

Phase analysis and structure refinements were carried out using X-ray powder diffraction data collected on diffractometers DRON-2.0M (Fe *K*α-radiation, angular range $20 \le 2\theta \le 120^{o}$, step 0.05º) and STOE Stadi P (Cu $K\alpha_1$-radiation, angular range $6\text{-}10 \le 2\theta \le 110^{o}$, step 0.015º). The profile and structural parameters were refined by the Rietveld method, using the program package FullProf Suite [19]. A single crystal was extracted from the alloy of composition $Hf_{50}Ga_{17}Si_{33}$. X-ray single-crystal diffraction data were collected in the φ-oscillation scan mode at room temperature on a Stoe IPDS-IIT diffractometer (Mo *K*α-radiation, λ = 0.71073 Å, graphite monochromator, imaging plate detector). An analytical absorption correction was applied using X-Shape/X-Red software [20,21]. The structures were solved by direct methods, using the program SHELXS-97 [22], and refined using the program SHELXL-97 [22] under the graphical user interface WinGX [23].

Results

Binary systems

The existence of 13 compounds at 600ºC in the boundary binary systems Hf–Ga and Hf–Si was confirmed. Crystallographic data for the binary compounds of the systems Hf–Ga and Hf–Si, including literature data and cell parameters refined in this work, are summarized in Table 1.

Table 1 Crystallographic data for the binary compounds of the systems Hf–Ga and Hf–Sn.

Compound	Structure type	Pearson symbol	Space group	Cell parameters, Å			Reference
				a	*b*	*c*	
$HfGa_3$	$TiAl_3$	*tI*8	*I*4/*mmm*	3.881	–	9.032	[24]
				3.87795(15)	–	9.0166(3)	[11]
$HfGa_2$	$HfGa_2$	*tI*24	$I4_1/amd$	4.046	–	25.446	[24]
				4.0408(5)	–	25.438(6)	[11]
Hf_2Ga_3	Zr_2Al_3	*oF*40	*Fdd*2	9.402	13.63	5.472	[24]
				9.4025(16)	13.632(3)	5.4696(8)	[11]
HfGa	ThIn	*oP*24	*Pbcm*	9.171	8.503	5.648	[25]
				9.1609(10)	8.5097(8)	5.6384(6)	[11]
$Hf_{11}Ga_{10}$	$Ho_{11}Ge_{10}$	*tI*84	*I*4/*mmm*	10.282	–	14.73	[26]
				10.2887(5)	–	14.7134(13)	[11]
Hf_5Ga_3	Mn_5Si_3	*hP*16	$P6_3/mcm$	7.970	–	5.686	[24]
				7.9601(10)	–	5.6779(8)	[11]
Hf_2Ga	$CuAl_2$	*tI*12	*I*4/*mcm*	6.690	–	5.294	[24]
				6.6815(19)	–	5.363(2)	[11]
$HfSi_2$	$ZrSi_2$	*oS*12	*Cmcm*	3.672	14.57	3.641	[14]
				3.6696(2)	14.5375(11)	3.6409(3)	this work
HfSi	FeB	*oP*8	*Pnma*	6.889	3.772	5.223	[14]
				6.8724(7)	3.7684(4)	5.2227(7)	this work
Hf_5Si_4	Zr_5Si_4	*tP*36	$P4_12_12$	7.039	–	12.83	[14]
				7.0343(8)	–	12.814(2)	this work
Hf_3Si_2	U_3Si_2	*tP*10	*P*4/*mbm*	6.988	–	3.675	[14]
				6.9864(6)	–	3.6677(3)	this work
Hf_5Si_3	Mn_5Si_3	*hP*16	$P6_3/mcm$	7.844	–	5.492	[14]
				7.8445(3)	–	5.4927(3)	this work
Hf_2Si	$CuAl_2$	*tI*12	*I*4/*mcm*	6.553	–	5.186	[27]
				6.5510(2)	–	5.1862(2)	this work

Isothermal section of the phase diagram of the system Hf–Ga–Si at 600ºC

The isothermal section of the phase diagram of the ternary system Hf–Ga–Si at 600ºC is shown on Fig. 1. It is constructed from 15 single-phase, 26 two-phase and 12 three-phase fields. Two continuous solid solutions form in the system, between the isostructural binary compounds Hf_5Ga_3 and Hf_5Si_3 (structure type Mn_5Si_3) and between Hf_2Ga and Hf_2Si (structure type $CuAl_2$). The other binary compounds of the systems Hf–Ga and Hf–Si do not dissolve noticeable amounts of the third component. One ternary compound of constant composition $HfGa_{0.33}Si_{0.67}$ was found at 600ºC [28]. It is characterized by the highest number of equilibria (9) in the system.

The ternary compound $HfGa_{0.33}Si_{0.67}$

The crystal structure of the ternary compound existing on the line with 50 at.% Hf was found to be different from the structures of the binary compounds HfGa (structure type ThIn) and HfSi (structure type FeB). It was studied by X-ray single-crystal diffraction. The ternary compound $HfGa_{0.33}Si_{0.67}$ crystallizes in the orthorhombic structure type TlI (Pearson symbol *oS*8, space group *Cmcm*, a = 3.7338(7), b = 9.889(2), c = 3.7441(7) Å) [28]. One of the two sites in Wyckoff position 4*c* is occupied by Hf atoms and the second one by a statistical mixture (*M*) of Ga and Si atoms in the ratio 1:2. Atomic coordinates and displacement parameters are listed in Table 2. The unit cell content and the coordination polyhedra of the atoms in the structure of $HfGa_{0.33}Si_{0.67}$ are shown on Fig. 2. The Hf atoms center 17-vertex polyhedra $\underline{Hf}M_7Hf_{10}$ (pentagonal prisms M_6Hf_4 with seven additional atoms above the faces). The atoms of the statistical mixture center 9-vertex polyhedra $\underline{M}M_2Hf_7$ (trigonal prisms Hf_6 with three additional atoms above the side faces).

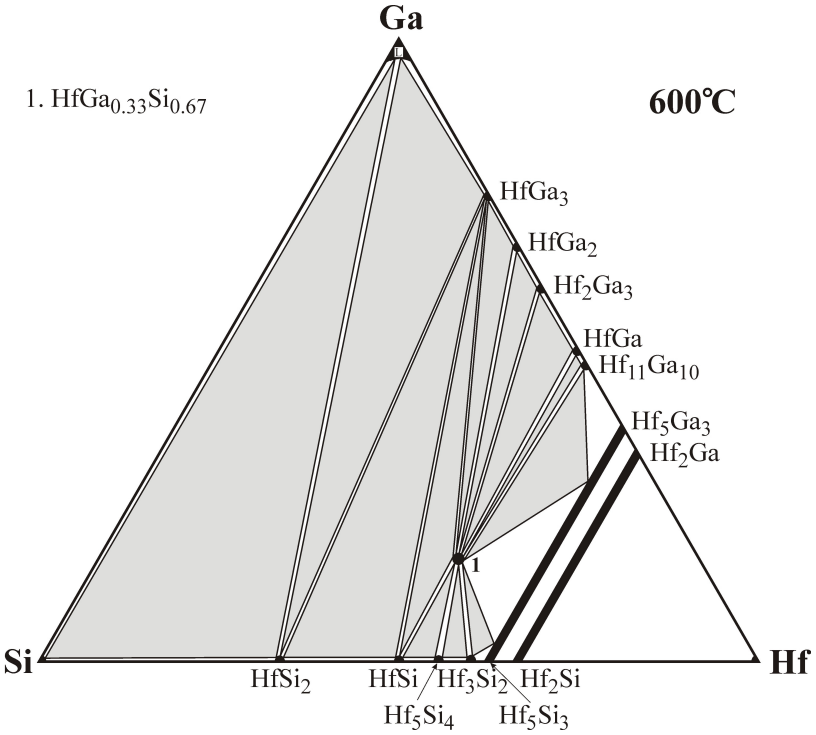

Fig. 1 Isothermal section of the phase diagram of the system Hf–Ga–Si at 600ºC.

Table 2 Atomic coordinates and displacement parameters (Å^2) for $HfGa_{0.33}Si_{0.67}$.

Site	Wyckoff position	*x*	*y*	*z*	U_{eq}
Hf	4*c*	0	0.35415(7)	¼	0.0109(5)
M[a]	4*c*	0	0.0813(4)	¼	0.0120(13)

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hf	0.0129(6)	0.0112(6)	0.0086(6)	0	0	0
M[a]	0.016(2)	0.0105(18)	0.0092(18)	0	0	0

[a] M = 0.33(2)Ga + 0.67(2)Si

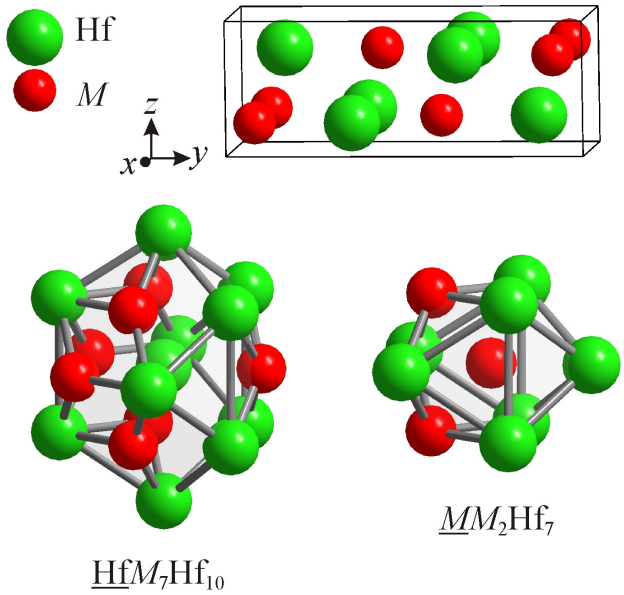

Fig. 2 Unit cell and coordination polyhedra of the atoms in the structure of $HfGa_{0.33}Si_{0.67}$.

Solid solution $Hf_5Ga_{3-x}Si_x$ (x = 0-3)

A continuous solid solution $Hf_5Ga_{3-x}Si_x$ (x = 0-3) forms between the binary compounds Hf_5Ga_3 and Hf_5Si_3 in the system Hf–Ga–Si along the line with 62.5 at.% Hf. It was studied by X-ray powder diffraction on 8 samples of different compositions. The solid solution $Hf_5Ga_{3-x}Si_x$ (x = 0-3) retains the structure of the limiting binary compounds: structure type Mn_5Si_3, Pearson symbol *hP*16, space group $P6_3/mcm$). The cell parameters within the solid solution decrease with increasing Si content (*a* = 7.9601(10)-7.8445(3), *c* = 5.6779(8)-5.4927(3) Å), which is in agreement with the smaller atomic radius of Si, compared to the atomic radius of Ga. The *a*- and *b*-parameters decrease by 1.45%, whereas the *c*-parameter decreases by 3.26%. The composition dependence of the cell parameters *versus* the Si content in $Hf_5Ga_{3-x}Si_x$ (*x* = 0-3) is shown on Fig. 3.

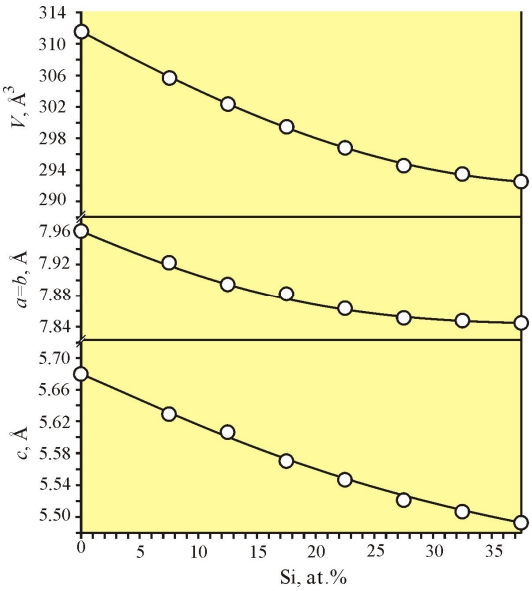

Fig. 3 Cell parameters as a function of the Si content in the solid solution $Hf_5Ga_{3-x}Si_x$ (x = 0-3).

Solid solution $Hf_2Ga_{1-x}Si_x$ (x = 0-1)

Along the line with 66.7 at.% Hf another continuous solid solution, $Hf_2Ga_{1-x}Si_x$ (x = 0-1), forms. It crystallizes with the structure type $CuAl_2$, like the limiting binary compounds Hf_2Ga and Hf_2Si. The cell parameters, refined from X-ray powder diffraction data, decrease with increasing Si content (*a* = 6.6815(19)-6.5510(2), *c* = 5.363(2)-5.1862(2) Å) within the solid solution. The *a*- and *b*-parameters decrease by 1.95%, whereas the *c*-parameter decreases by 3.30%. The composition dependence of the cell parameters *versus* the Si content in $Hf_2Ga_{1-x}Si_x$ (x = 0-1) is shown on Fig. 4.

Discussion

The Hf-rich region of the phase diagram of the ternary system Hf–Ga–Si at 600ºC is characterized by the existence of continuous solid solutions between isostructural binary compounds of the Hf–Ga and Hf–Si systems. The formation of similar continuous solid solutions has been reported for related systems: $Zr_2Al_{1-x}Si_x$ (x = 0-1) with $CuAl_2$-type structure in the Zr–Al–Si system at 1200ºC [2] and $Hf_5Ga_{3-x}Ge_x$ (x = 0-3) with Mn_5Si_3-type structure in the Hf–Ga–Ge system at 600ºC [28]. Obviously, the small difference

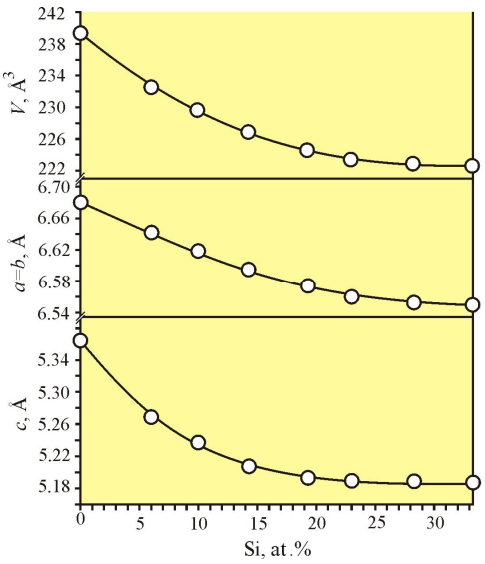

Fig. 4 Cell parameters as a function of the Si content in the solid solution $Hf_2Ga_{1-x}Si_x$ (x = 0-1).

between the atomic radii of the *p*-block elements, with respect to the size of the Hf atoms, does not influence significantly the crystal structures of the phases in the Hf-rich part of the system Hf–Ga–Si. On the contrary, the Hf-poor region of the phase diagram of the ternary system Hf–Ga–Si at 600ºC is characterized by the absence of isostructural binary compounds in the systems Hf–Ga and Hf–Si and by negligible solubility of the third component in the binary compounds. In this part of the system, the *p*-block elements dominate the formation of phases, *i.e.* the difference between Ga and Si is pronounced and results in different numbers and stoichiometry of the binary compounds and different crystal structures of isostoichiometric binary phases.

The only ternary compound in the system Hf–Ga–Si at 600ºC is formed in the quasibinary system HfGa–HfSi. The ternary phase is dominating in the formation of two-phase equilibria in the system: it is in equilibrium with six (out of seven) binary compounds of the Hf–Ga system and with four (out of six) binary compounds of the Hf–Si system. The crystal structure of $HfGa_{0.33}Si_{0.67}$ (structure type TlI) is closely related to the structure of the binary compound HfSi (structure type FeB), since both structure types are the members of the same homologous series [29]. In the structure of $HfGa_{0.33}Si_{0.67}$ trigonal prisms formed by Hf atoms and centered by the atoms of a statistical mixture of *p*-block elements are joined *via* triangular faces and two of the three square faces, forming walls perpendicular to the *y*-axis. Neighboring walls are separated by empty tetragonal pyramids and tetrahedra formed by Hf atoms. The atoms of the *p*-block elements form infinite zigzag chains along the *z*-axis. An isostructural ternary compound, $ZrGa_{0.66-0.90}Si_{0.34-0.10}$, was found in the system Zr–Ga–Si at 800ºC [4]. In contrast to the ternary phase in the system Hf–Ga–Si, the ternary compound in the system Zr–Ga–Si is characterized by a pronounced homogeneity range (12 at.%) and is considered to be a Si-stabilized high-temperature modification of the binary compound ZrGa.

In contrast to the ternary system Hf–Ga–Sn [11], no tendency towards ordering of the atoms of *p*-block elements is observed in the structures of the ternary phases of the system Hf–Ga–Si. The larger difference between the atomic radii of Ga and Sn, with respect to the difference between the sizes of Ga and Si atoms, may be responsible for this behavior.

Conclusions

The ternary system Hf–Ga–Si at 600ºC is characterized by the existence of two continuous solid solutions in the Hf-rich corner, $Hf_5Ga_{3-x}Si_x$ (x = 0-3, structure type Mn_5Si_3) and $Hf_2Ga_{1-x}Si_x$ (x = 0-1, structure type $CuAl_2$), and one ternary compound, $HfGa_{0.33}Si_{0.67}$ (structure type TlI), in the quasibinary system HfGa–HfSi. No tendency towards ordering of the Ga and Si atoms is observed in the structures of the ternary phases.

Acknowledgements

This work was supported by Ministry of Education and Science, Youth and Sport of Ukraine under the grants No. 0112U001279 and No. 0112U001280.

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