PHASE EQUILIBRIA IN THE {Zr, Hf}-Ag-Al SYSTEMS AT 500°C AND CRYSTAL STRUCTURE OF THE TERNARY COMPOUNDS

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ABSTRACT

The phase equilibria at 500°C in the {Zr, Hf}-Ag-Al systems have been investigated in the whole concentration region. Three ternary compounds were found to occur in each of the systems: $ZrAg_{0.32}Al_{2.68}$ ($AuCu_3$ structure type, space group $Pm\bar{3}m$, a=0.41016(1) nm), $ZrAg_{0.16-0.31}Al_{1.84-1.69}$ ($MgCu_2$ str. type, sp. gr. $Fd\bar{3}m$, a=0.75147(1)-0.75258(1) nm), $Zr_6Ag_{1.30-1.82}Al_{5.70-5.18}$ (W_6Fe_7 str. type, sp. gr. $R\bar{3}m$, a=0.54017(3)-0.54072(3) nm, c=2.9021(5)-2.9055(3) nm); $HfAg_{0.28-0.43}Al_{1.72-1.57}$ ($MgCu_2$ str. type, sp. gr. $Fd\bar{3}m$, a=0.74600(2)-0.74631(3) nm), $Hf_6Ag_{0.39-1.43}Al_{6.61-5.57}$ (W_6Fe_7 str. type, sp. gr. $R\bar{3}m$, a=0.53098(3)-0.53375(3) nm, c=2.9151(2)-2.9086(3) nm), $Hf_4Ag_{1.10}Al_{1.90}$ (Zr_4Al_3 str. type, sp. gr. $P\bar{6}$, a=0.5332(1) nm, c=0.54279(7) nm). The crystal structure of these aluminides was studied using X-ray powder and single crystal diffraction data.

INTRODUCTION

Aluminides of 4a-metals possess valuable physical and chemical (relatively high melting point, low density, oxidation resistance) and mechanical (hardness, strenght, lightness, high corrosion-resistivity) properties [1, 2]. There is considerable interest in intermetallics of silver for their electrical properties [3]. Therefore, investigation of interaction between the components in the {Zr, Hf}-Ag-Al ternary systems will result in revealing new intermetallic compounds. Some of them may be of interesting for practical application.

Phase diagrams of the {Zr, Hf}-Al, {Zr, Hf}-Ag, Ag-Al boundary binary systems are studied and presented in Refs. [4-7].

Phase equilibria in the {Zr, Hf}-Ag-Al ternary systems are not studied to date. Previous investigations of separate alloys revealed the existence of the $ZrAg_{0.32}Al_{2.68}$ ($AuCu_3$ structure type) and $ZrAg_{0.16}Al_{1.84}$ ($MgCu_2$ structure type) ternary compounds [8]. Among the M-Ag-X related ternary systems, where M=Ti, Zr, Hf; X=Al, Ga, In, only the Ti-Ag-Al [9], Zr-Ag-Ga [10], Zr-Ag-In [11] and Hf-Ag-Ga [12] systems have been studied. Five ternary compounds were found in these systems: $Ti_xAg_yAl_{100-x-y}$ ($25 \le x \le 30$, $8 \le y \le 14$) ($AuCu_3$ structure type), $ZrAg_{0.5-0.6}Ga_{2.5-2.4}$ ($AuCu_3$), $ZrAg_{0.4}In_{2.6}$ ($AuCu_3$), Zr_5AgIn_3

(Hf_5CuSn_3), $HfAg_{0.72-0.85}Ga_{2.28-2.15}$ ($AuCu_3$). This study was carried out to investigate the isothermal sections of the {Zr, Hf}-Ag-Al phase diagrams, to synthesize new ternary compounds, to determine their crystal structure and to evaluate regularities of interaction of 4a-elements with 3b-elements and Ag.

EXPERIMENTAL

40 binary and 183 ternary samples were prepared by arc-melting of initial components under high purity argon on a water-cooled copper hearth. Starting materials were used in the form of pieces of high purity metals (Zr 99.95 wt.%, Hf 99.99 wt.%, Ag 99.99 wt.%, Al 99.997 wt.%). The samples were remelted twice for better homogenation. The alloys were afterwards sealed in evacuated quartz tubes and annealed at 500°C for 500-1000h. After heat treatment the samples were quenched by submerging the silica tubes in cold water.

Phase analysis was carried out by using X-ray powder films obtained in RKD-57.3 chambers (CrK-radiation) and diffractograms (diffractometers DRON-2.0, FeKa-radiation; DRON-3M, CuKa-radiation; HZG-4a, CuKa-radiation). The $M_6Ag_xAl_{7-x}$ aluminides were investigated by using single crystal X-ray diffraction (camera RKV-86, MoK- and CuK-radiation; diffractometer KUMA/Oxford KM4, MoKa-radiation). Precise lattice parameters and standart deviations were derived by least-square refinement using CSD softwave [13] and FullProf program [14].

RESULTS

Boundary binary systems

The existence of 19 binary compounds at 500°C has been confirmed: $ZrAl_3$ ($ZrAl_3$ structure type), $ZrAl_2$ ($MgZn_2$), Zr_2Al_3 (Zr_2Al_3), ZrAl (CrB), Zr_4Al_3 (Zr_4Al_3), Zr_3Al_2 (Zr_3Al_2), Zr_2Al ($InNi_2$), Zr_3Al ($AuCu_3$), $HfAl_3$ ($ZrAl_3$), $HfAl_2$ ($MgZn_2$), Hf_2Al_3 (Zr_2Al_3), HfAl (CrB), Hf_3Al_2 (Zr_3Al_2), Hf_5Al_3 (Mn_5Si_3), ZrAg (TiCu), Zr_2Ag ($MoSi_2$), HfAg (TiCu), Hf_2Ag ($MoSi_2$), Ag_2Al (Mg) [7]. Two other compounds exist in the limited temperature regions: Ag_3Al (β) (W structure type) exists above 603°C and Ag_3Al (μ) (βMn) is stable up to 450°C. In the Zr-Al system Zr_5Al_3 (W_5Si_3) and Zr_5Al_4 (Ti_5Ga_4) aluminides are stable above ~1000°C. The binary aluminides Hf_4Al_3 (Zr_4Al_3) and Hf_2Al (Al_2Cu) were not found to occur at 500°C.

Zr-Ag-Al ternary system

Isothermal section at 500°C of the Zr-Ag-Al phase diagram is presented in Fig.1.

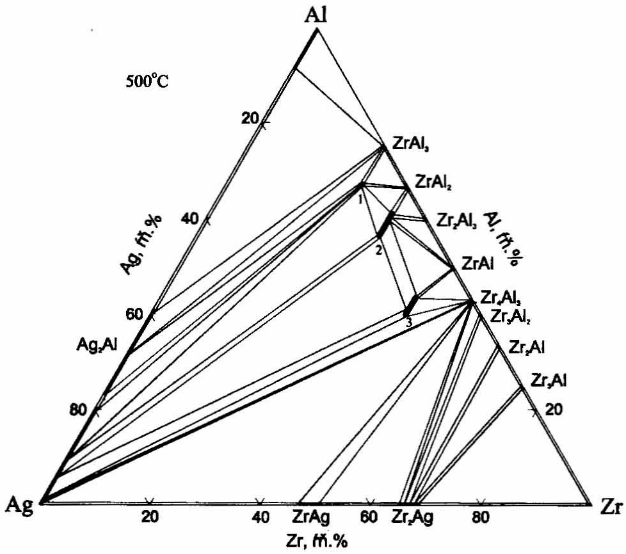

Figure 1. Zr-Ag-Al isothermal section at 500°C. Ternary compounds: (1) $ZrAg_{0.32}Al_{2.68}$; (2) $ZrAg_{0.16-0.31}Al_{1.84-1.69}$; (3) $Zr_6Ag_{1.30-1.82}Al_{5.70-5.18}$

Practically no solubility of third components in the binary compounds was observed. Three ternary compounds were found in this system. The crystal structure of the $ZrAg_{0.32}Al_{2.68}$ ($AuCu_3$ structure type) and $ZrAg_{0.16}Al_{1.84}$ ($MgCu_2$) was reported earlier [8]. The latter compound has a homogeneity region, which extends from 5 to 10 at.% of Ag along the 33.3 at.% Zr isoconcentrate. These aluminides were also detected in cast and in homogenated at 800°C alloys. The lattice paremeters of the compounds are presented in Table 1.

Table 1. Crystal structure data of the {Zr, Hf}-Ag-Al ternary compounds

Compound	Structure type	Space group	Lattice parameters (nm)		Ref.
			a	c	
$ZrAg_{0.32}Al_{2.68}$	$AuCu_3$	Pm3m	0.41016(1)		[8]
$ZrAg_{0.16-0.31}Al_{1.84-1.69}$	$MgCu_2$	Fd3m	0.75147(1)- -0.75258(1)		[8], *
$Zr_6Ag_{1.30-1.82}Al_{5.70-5.18}$	W_6Fe_7	R3m	0.54017(3)- -0.54072(3)	2.9021(5)- -2.9055(3)	*
$HfAg_{0.28-0.43}Al_{1.72-1.57}$	$MgCu_2$	Fd3m	0.74600(2)- -0.74631(3)		*
$Hf_6Ag_{0.39-1.43}Al_{6.61-5.57}$	W_6Fe_7	R$\bar{3}$m	0.53098(3)- -0.53375(3)	2.9151(2)- -2.9086(3)	*
$Hf_4Ag_{1.10}Al_{1.90}$	Zr_4Al_3	P$\bar{6}$	0.5332(1)	0.54279(7)	*

* this work

The X-ray patterns of the samples containing 45-50 at.% Zr indicated the existence of unknown ternary compound. A single crystal was extracted from the cast alloy with a composition $Zr_{50}Ag_5Al_{45}$. Preliminary X-ray structure investigation showed that the crystal was of rhomboedric symmetry with lattice parameters a=0.5393(1) nm, c=2.9092(7) nm. These data indicated to the W_6Fe_7 structure type. The following X-ray structure refinement confirmed this supposition. Composition of the single crystal was determined as Zr_6AgAl_6 (=$Zr_{46.15}Ag_{6.86}Al_{46.98}$). Crystallographic data for the Zr_6AgAl_6 are listed in Table 2.

Table 2. X-ray experimental details and crystallographic data for the Zr_6AgAl_6

Structure type	W_6Fe_7
Space group	$R\bar{3}m$
a (nm)	0.5393(1)
c (nm)	2.9092(7)
Cell volume (nm^3)	0.7328(4)
F(000) (electrons)	1084
Number of atoms in the unit cell	39.0
Calculated density (g/cm^3)	5.495(3)
Absorption coefficient (1/cm)	729.11
Radiation and wavelenght (nm)	Mo, 0.70930
Diffractometer	KM-4
Mode of refinement	F(hkl)
Restrictions	F(hkl) > 4.00sig(F)
Weighing scheme	Unit
Number of atomic sites	5
Number of refined parameters	18
Two-theta and sinT/l (max)	102.96, 1.103
Number of measured reflections	5080
R_F	0.0667
Scale factor	0.741(3)
Calculated composition Zr, Ag, Al, at.%	46.15, 6.86, 46.98

It`s final atomic coordinates and displacement parameters are presented in Tables 3-4.

Table 3. Atomic coordinates and displacement parameters for Zr_6AgAl_6

Atoms	Site	x	y	z	B_{iso}
M1	18h	0.8345(5)	-x+1	0.2582(1)	0.6(1)
Zr1	6c	0	0	0.1659(1)	0.52(6)
Zr2	6c	0	0	0.3506(1)	0.76(6)
Zr3	6c	0	0	0.4546(1)	0.61(6)
M2	3a	0	0	0	1.0(2)

M1= 0.084(4)Ag + 0.916(4)Al
M2= 0.38(1)Ag + 0.62(1)Al.

Table 4. Anisotropic displacement parameters for Zr_6AgAl_6

Atoms	B11	B22	B33	B12	B13	B23
M1	0.6(1)	B11	0.8(2)	0.4(1)	0.0(1)	- B13
Zr1	0.45(7)	B11	0.7(1)	1/2B11	0	0
Zr2	0.67(7)	B11	0.9(1)	1/2B11	0	0
Zr3	0.66(7)	B11	0.5(1)	1/2B11	0	0
M2	0.5(2)	B11	2.0(3)	1/2B11	0	0

The annealed at 500°C alloy of the composition $Zr_{46}Ag_7Al_{47}$ was unhomogeneous. X-ray analysis of the annealed at 500°C alloys on the section of 46 at.% Zr showed, that the homogeneity region of this ternary compound extends from 10 to 14 at.% Ag, i.e. it's composition is as follows $Zr_6Ag_{1.30-1.82}Al_{5.70-5.18}$. This discrepancy between stoichiometries of ternary compound $Zr_6Ag_xAl_{7-x}$ obtained by X-ray single crystal and powder analyses indicated different homogeneity region of this compound at different temperatures. But this conclusion should be confirmed experimentally.

Hf-Ag-Al ternary system

Interaction between the components in the Hf-Ag-Al system is similar to that in the Zr-Ag-Al system. Isothemal section at 500°C of the Hf-Ag-Al phase diagram is presented in Fig. 2.

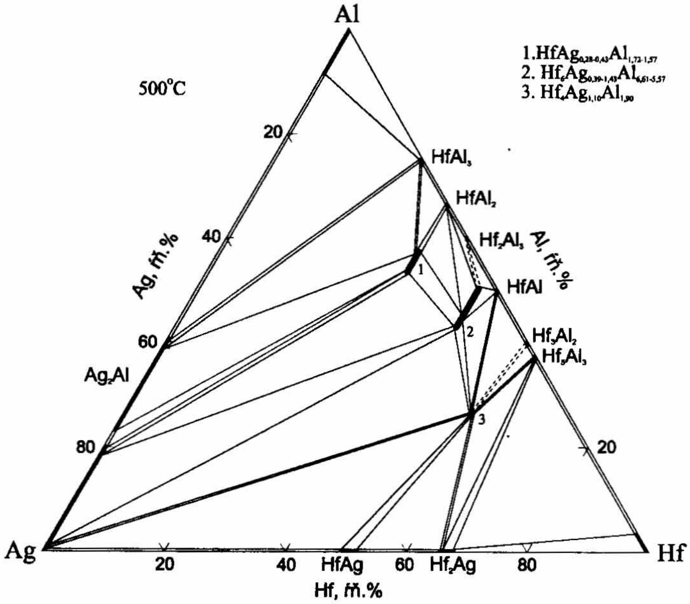

Figure 2. Hf-Ag-Al isothermal section at 500°C. Ternary compounds: (1) $HfAg_{0.28-0.43}Al_{1.72-1.57}$; (2) $Hf_6Ag_{0.39-1.43}Al_{6.61-5.57}$; (3) $Hf_4Ag_{1.10}Al_{1.90}$

Two ternary compounds isotypic with $MgCu_2$ and W_6Fe_7 were found to occur: $HfAg_{0.28-0.43}Al_{1.72-1.57}$ and $Hf_6Ag_{0.39-1.43}Al_{6.61-5.57}$ (Table 1). The crystal structure of the first one was investigated by means of profile analysis of X-ray powder pattern (Fig.3).

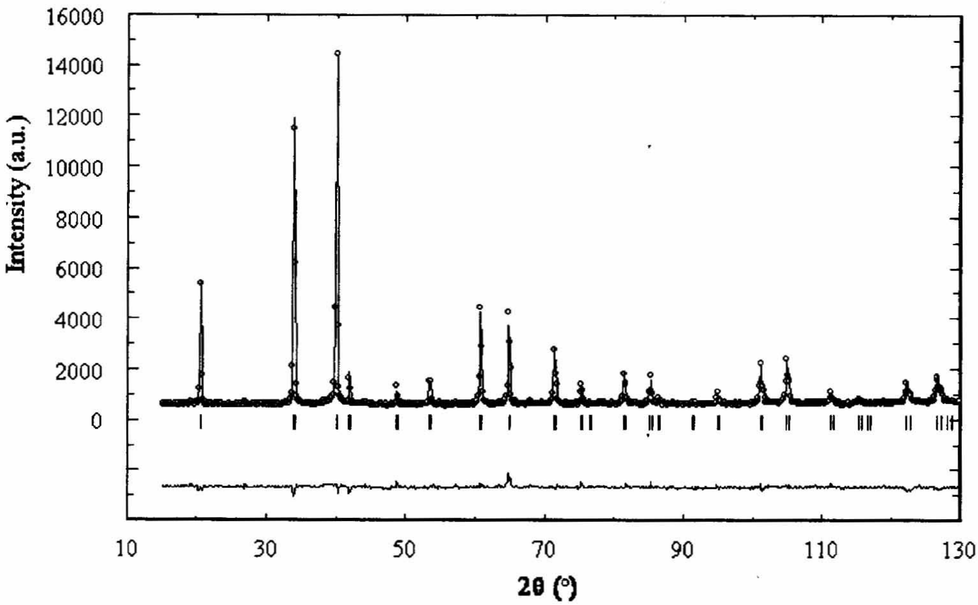

Figure 3. Results or the Rietveld refinement of the $HfAg_{0.43}Al_{1.57}$ (observed (dots), calculated (line) and difference (bottom) profiles).

The sructure was refined for the sample of the nominal composition $Hf_{33.3}Ag_{14}Al_{52.7}$ (=$HfAg_{0.43}Al_{1.57}$). Atomic coordinates and isotropic temperature parameters are given in Table 5.

Table 5. Atomic coordinates and isotropic temperature parameters for the $HfAg_{0.43}Al_{1.57}$ compound (structure type $MgCu_2$, $Fd\bar{3}m$ space group, a=0.74631(3) nm, R_p=4.14%, R_{wp}=5.47%)

Atoms	**Site**	**X**	**y**	**z**	B_{iso}
Hf	8a	0	0	0	0.44(5)
M	16d	5/8	5/8	5/8	1.5(1)

M = 3.4(1)Ag + 12.6(1)Al.

The $Hf_6Ag_xAl_{7-x}$ ternary compound was investigated by single crystal X-ray diffraction (first stage) and X-ray powder analysis (final stage). The XRD data of the $Hf_{46}Ag_{10}Al_{44}$ (=$Hf_6Ag_{1.28}Al_{5.72}$) sample were refined in approximation of W_6Fe_7 structure type with the lattice parameters a = 0.53338(1), c=2.9075(1) nm, space group $R\bar{3}m$ (R_I = 8.02%). Atomic coordinates and isotropic temperature parameters are given in Table 6.

Table 6. Atomic coordinates and isotropic temperature parameters for the $Hf_6Ag_{1.28}Al_{5.72}$ compound (structure type W_6Fe_7, $R\bar{3}m$ space group, a=0.53338(1) nm, c=2.9075(1) nm, R_I=8.02%).

Atoms	Site	X	y	z	B_{iso}
M1	18h	0.8338(8)	-x+1	0.2581(2)	1.0(1)
Hf1	6c	0	0	0.1656(1)	0.70(4)
Hf2	6c	0	0	0.3506(1)	0.91(5)
Hf3	6c	0	0	0.4541(1)	0.96(5)
M2	3a	0	0	0	0.8(1)

M1=0.139(4)Ag + 0.861(4)Al
M2=0.45(1)Ag + 0.55(1)Al.

Results of the Rietveld profile refinement of the $Hf_6Ag_{1.28}Al_{5.72}$ XRD data are in Fig. 4.

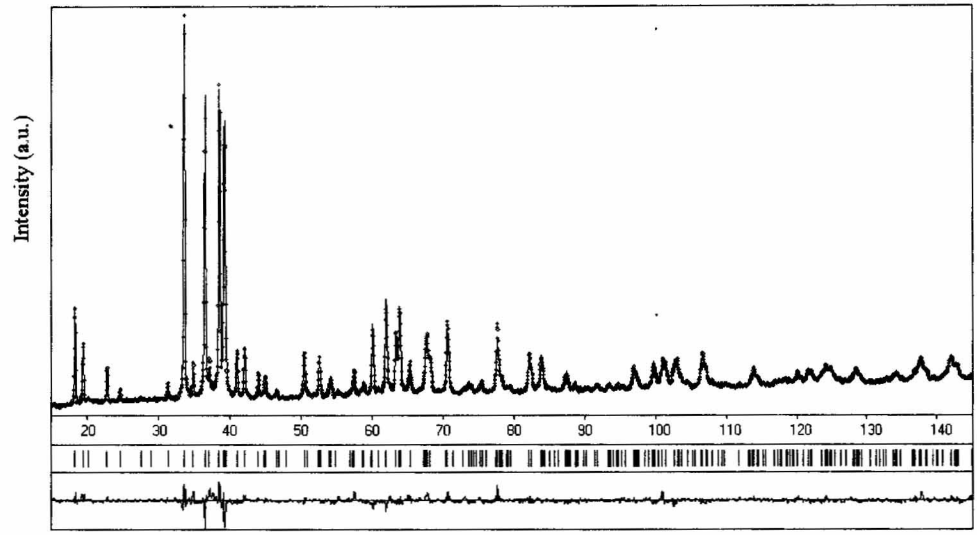

Figure 4. Results or the Rietveld refinement of the $Hf_6Ag_{1.28}Al_{5.72}$ (observed (dots), calculated (line) and difference (bottom) profiles).

One more ternary compound $Hf_4Ag_{1.10}Al_{1.90}$ was synthesised in the system. It`s crystal structure was determined from two phases` alloy of the composition $Hf_{57}Ag_{14}Al_{29}$. The binary compound Hf_5Al_3 was the second phase which was present in the sample. The XRD data were indexed on the basis of a hexagonal lattice with the a=0.5332(1), c=0.54279(7) nm parameters. The observed intensities were corroborated by calculation assuming this phase to have Zr_4Al_3-type crystal structure (space group $P6$) with the final residuals R_p=3.69%, R_{wp}=4.90%. Atomic coordinates and isotropic temperature parameters are given in Table 7.

Table 7. Atomic coordinates and isotropic temperature parameters for the $Hf_4Ag_{1.10}Al_{1.90}$ compound (structure type Zr_4Al_3, space group $P\bar{6}$, a=0.5332(1) nm, c=0.54279(7) nm, R_p=3.69%, R_{wp}=4.90%).

Atoms	Site	x	y	z	B_{iso}
Hf1	1b	0	0	1/2	0.43(8)
Hf2	1f	2/3	1/3	1/2	0.43(8)
Hf3	2h	1/3	2/3	0.259(1)	0.43(8)
M	3j	0.291(5)	0.180(5)	0	0.43(8)

M=1.10(5)Ag + 1.90(5)Al

CONCLUSIONS

Analysis of phase equilibria in the M-Ag-X (M=Ti, Zr, Hf; X=Al, Ga, In) systems and compositions of the compounds and their crystal structures led to the following conclusions:

1. In all investigated M-Ag-X systems the ternary compounds occur up to 21 at.% Ag.
2. The {Zr, Hf}-Ag-Al and Zr-Ag-In systems are the complexest ones in contrast to the Ti-Ag-Al, {Zr, Hf}-Ag-Ga systems. Only one ternary compound occurs in each of the latter systems.
3. Formation of the ternary phases with the $AuCu_3$ structure type is typical for all investigated systems. These compounds have homogeneity ranges in Ti-Ag-Al, {Zr, Hf}-Ag-Ga systems. In the Zr-Ag-{Al, In} systems these compounds occur at constant compositions.
4. The ternary compounds belonging to the $MgCu_2$, W_6Fe_7 and Zr_4Al_3 structure types exist only in the {Zr, Hf}-Ag-Al systems.

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