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Crystal structure of Hf_6PtAl_2 and comparison with HfPtAl

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The Hf_6PtAl_2 and HfPtAl compounds have been synthesized by arc-melting followed by heat treatment at 800°C for ten days. These intermetallics crystallize with hexagonal symmetry and have the lattice parameters a = 7.9054(3) Å, c = 3.3438(1) Å (space group $P\bar{6}2m$) for Hf_6PtAl_2 and a = 7.09197(8) Å, c = 7.1152(1) Å (space group $P\bar{6}2c$) for HfPtAl.

Hafnium platinum aluminide / Crystal structure / X-ray powder diffraction

1. Introduction

Some of the Hf-*d*-metal-Al systems show the existence of intermetallic compounds with different superstructures of the Fe_2P type. Markiv *et al.* [1,2] found the equiatomic compound HfNiAl and the ternary compounds Hf_6MAl_2 (M = Fe, Co, Ni), which crystallize with the ZrNiAl and Zr_6CoGa_2 (anti-K_2UF_6) structure types, respectively. Both structures are ordered variants of the Fe_2P type (*i.e.* $Fe_3^{(1)}\,Fe_3^{(2)}\,P_2^{(3)}\,P_1^{(4)}$): $Al_3^{(1)}\,Zr_3^{(2)}\,Ni_2^{(3)}\,Ni_1^{(4)}$ for ZrNiAl and $Zr_3^{(1)}\,Zr_3^{(2)}\,Ga_2^{(3)}\,Co_1^{(4)}$ for Zr_6CoGa_2. In our previous paper [3] we have shown that the related ZrPtAl and HfPtAl compounds belong to the HfRhSn type (*i.e.* $Hf_6^{(1)}\,Sn_6^{(2)}\,Rh_4^{(3)}\,Rh_2^{(4)}$), a superstructure of Mg_2Ga (*i.e.* $Mg_6^{(1)}\,Mg_6^{(2)}\,Ga_4^{(3)}\,Ga_2^{(4)}$). The latter is a deformed variant of the ZrNiAl (Fe_2P) type [4]. In this paper we report the results of the crystal structure investigation of a new compound, Hf_6PtAl_2. For the purpose of comparison we also reinvestigated the structure of the HfPtAl intermetallic, which was synthesized under the same conditions as Hf_6PtAl_2.

2. Experimental details

Starting materials for the preparation of Hf_6PtAl_2 and HfPtAl were hafnium chips, platinum sheets and gallium tear drops, all with purities higher than 99.9 wt.%. The samples were prepared directly from the elements by arc-melting under an argon atmosphere (with a titanium pellet as a getter) on a water-cooled copper hearth. The products were turned over and re-melted at least three times in order to ensure homogeneity. After arc-melting the mass losses were below 0.5 wt.%. The as-prepared alloys were wrapped in tantalum foil, sealed in evacuated quartz tubes and annealed at 800 ºC for 10 days. After the heat treatment the samples were quenched by submerging the quartz tubes in cold water.

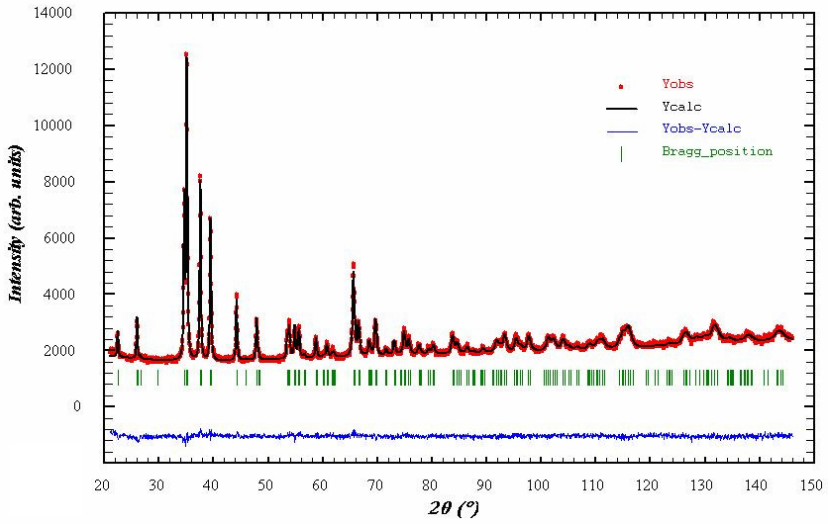
Phase analysis of the alloys was carried out using X-ray powder diffraction (XRD) patterns obtained on a DRON-2.0 diffractometer with Fe K_α-radiation. Another powder diffractometer, HZG-4a with Cu K_α-radiation, was used for the crystal structure determination of the investigated intermetallic compounds. The patterns were recorded in the $\theta/2\theta$ mode with the following parameters: 2θ region 15-145º, step scan 0.05º, counting time per step 20 s. Theoretical powder patterns were calculated using PowderCell [5]. The refinement of the crystal structure was performed by means of the Rietveld method using the program FullProf [6]. A pseudo-Voigt profile shape function was used. The background was refined with a 6th order polynomial function.

3. Results and discussion

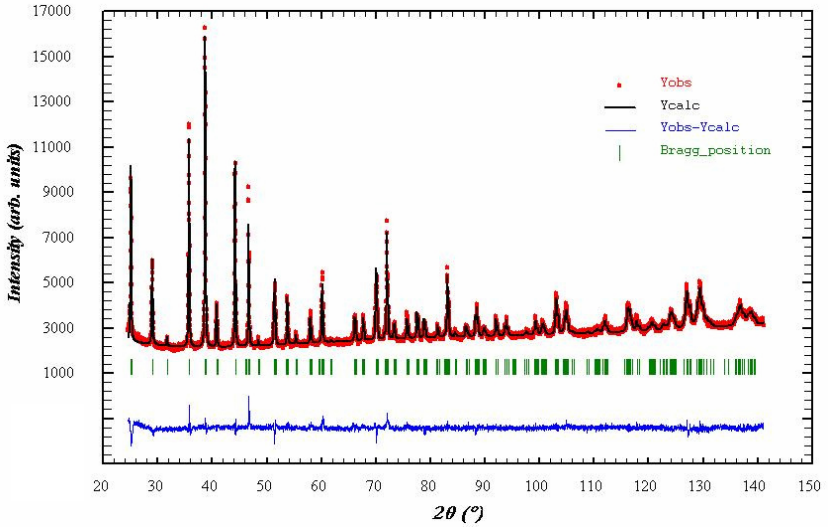
From X-ray phase analyses of samples annealed at 800ºC a new ternary compound with the composition Hf_6PtAl_2 was found in the Hf-rich corner of the Hf–Pt–Al system. Indexing of the XRD pattern showed that this compound is hexagonal with lattice parameters a = 7.9054(3) and c = 3.3438(1) Å. The analysis of the chemical composition of the alloy and the intensities of the Bragg peaks in the pattern

Table 1 Crystal data and details of the structural refinement of HfPtAl and Hf_6PtAl_2.

Compound	Hf_6PtAl_2	HfPtAl
Prototype	Zr_6CoGa_2	HfRhSn
Space group, Z	$P\bar{6}2m$ (# 189), 1	$P\bar{6}2c$ (# 190), 6
Pearson symbol	*hP*9	*hP*18
Unit cell parameters:		
a, Å	7.9054(3)	7.09197(8)
c, Å	3.3438(1)	7.1152(1)
V, Å^3	180.98(1)	309.921(8)
c/*a* or 2*c*/*a*	0.846	1.003
Calculated density, g/cm^3	12.111	12.877
Reliability factors:		
R_B	0.0472	0.0654
R_F	0.0296	0.0459
R_p	0.0194	0.0228
R_{wp}	0.0248	0.0320
Goodness of fit	1.17	1.71



(a)

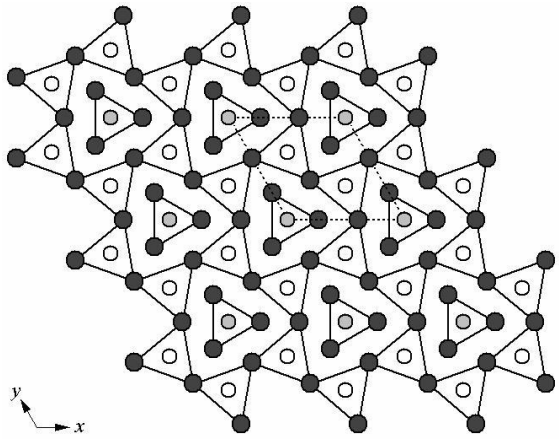


(b)

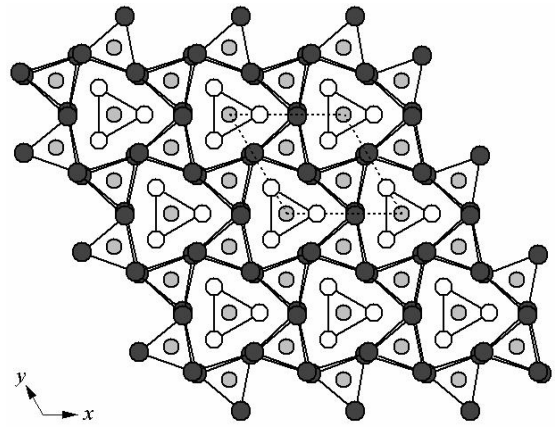
Fig. 1 Results of the Rietveld profile refinement of the X-ray diffraction data for the ternary compounds Hf_6PtAl_2 (a) and HfPtAl (b). Experimental data are represented by dots, calculated profiles by a red line and the difference between observed and calculated intensities as a blue line at the bottom. Vertical bars represent calculated positions of the Bragg peaks.

indicated the Zr_6CoGa_2 structure type. A consecutive Rietveld refinement confirmed this finding. We also reinvestigated the crystal structure of the HfPtAl compound. For samples quenched either from 600ºC or 800ºC, a HfRhSn-type structure was found. Its lattice parameters agreed with those published earlier [3]. Crystallographic data and final reliability factors of the structure refinements for Hf_6PtAl_2 and HfPtAl are listed in Table 1. The resulting atomic coordinates and displacement parameters are presented in Table 2. Results of the Rietveld profile refinement of the above mentioned compounds are shown in Fig. 1.

Unit cells and arrangements of trigonal prisms in Hf_6PtAl_2 and HfPtAl are presented in Fig. 2. In the structure of Hf_6PtAl_2, the platinum and aluminium atoms are located at the centers of undistorted trigonal prisms formed only by hafnium atoms, while in the structure of HfPtAl the platinum atoms are located in two kinds of trigonal prism, *i.e.* in undeformed prisms built by Al atoms and slightly distorted prisms composed of Hf atoms.



(a)



(b)

Fig. 2 Projections of the structures of Hf_6PtAl_2 (a) and HfPtAl (b) on the *xy* plane. Black circles indicate Hf atoms, grey filled circles are Pt atoms, and Al atoms are represented by white circles. The unit cells are shown using dotted lines.

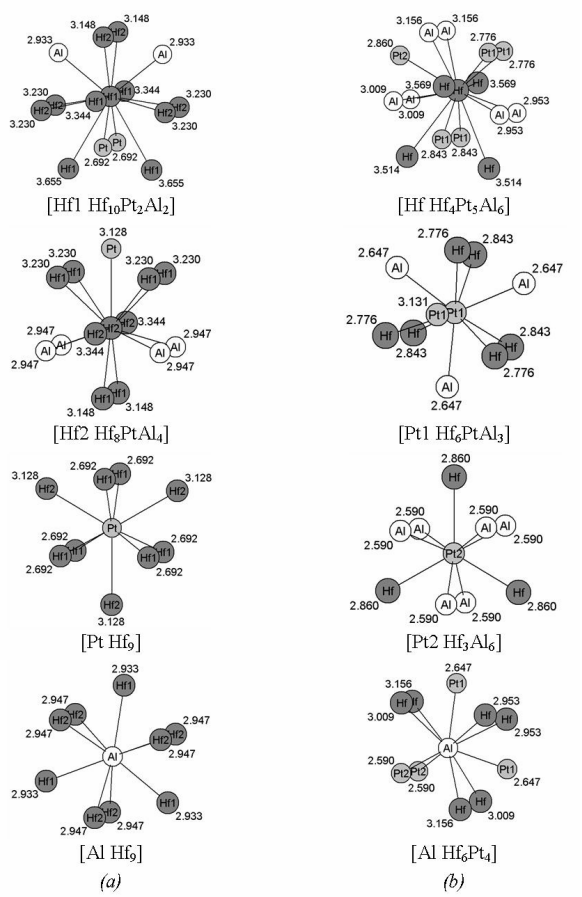


Fig. 3 Nearest-neighbor environments in the structures of Hf_6PtAl_2 (a) and HfPtAl (b). Coordination polyhedra of the central atoms are indicated. Interatomic distances are shown in Å.

Atom coordinations and interatomic distances are presented in Fig. 3. The shortest Hf-Hf contacts occur in the structure of Hf_6PtAl_2, being equal to 3.148 Å, which is smaller than the shortest Hf-Hf atomic distance (3.18 Å) in hafnium metal [7]. In the structure of HfPtAl the shortest Hf-Hf contact is much greater and reaches 3.514 Å. The shortest Hf-Pt and Hf-Al distances are slightly smaller than the sum of r_{Hf} and r_{Pt} (r_{Al}): $d_{Hf\text{-}Pt}$ = 2.692 Å and $d_{Hf\text{-}Al}$ = 2.933 Å for Hf_6PtAl_2, $d_{Hf\text{-}Pt}$ = 2.776 Å and $d_{Hf\text{-}Al}$ = 2.953 Å for HfPtAl, respectively. For comparison, $r_{Hf} + r_{Pt}$ = 2.97 Å and $r_{Hf} + r_{Al}$ = 3.02 Å using values from [7]. The Pt-Pt bonds are longer than the distances in *ccp* platinum. Contacts between Pt and Al are found only in the structure of HfPtAl ($d_{Pt\text{-}Al}$ = 2.590 Å), and the distances are shorter than the sum of r_{Pt} and r_{Al}, according the data from [7].

To conclude, considering the results of this work and earlier published papers [1-3], six ternary compounds with Zr_6CoGa_2 and ZrNiAl (or HfRhSn) structure types have been found in the Hf-{Fe, Co, Ni, Pt}-Al systems. Their structures are closely related

Table 2 Atomic coordinates and isotropic displacement parameters for HfPtAl and Hf_6PtAl_2.

Atom	Site	*x*	*y*	*z*	B_{iso}, Å^2
Hf_6PtAl_2					
Hf1	3*g*	0.2669(2)	0	½	1.00(5)
Hf1	3*f*	0.6043(2)	0	0	1.10(5)
Pt	1*a*	0	0	0	0.5(2)
Al	2*d*	⅓	⅔	½	1.15(6)
HfPtAl					
Hf	6*h*	0.4141(3)	0.3914(3)	¼	0.41(3)
Pt1	4*f*	⅓	⅔	0.0300(3)	0.71(3)
Pt2	2*b*	0	0	¼	0.58(5)
Al	6*g*	0.265(1)	0	0	0.6(2)

and can be obtained from the hexagonal AlB_2 type of structure [4,8].

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