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The Crystal Structures of Two Modifications of $HfNi_3$

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$HfNi_3$ occurs in two modifications: a high-temperature α form, stable from its melting point to 1200 °C, and a low-temperature β form, stable below 1200 °C. The crystal structures of the two modifications have been determined from single-crystal X-ray diffraction data. α-$HfNi_3$ crystallizes with the $BaPb_3$-type structure, space group $R\bar{3}m$ (No. 166). The parameters of the triply-primitive hexagonal unit cell are $a = 5{\cdot}2787$ (1), $c = 19{\cdot}2324$ (10) Å at room temperature. The structure can be described as a stacking of nine triangularly ordered, close-packed AB_3 layers in the sequence *ABABCBCAC*. β-$HfNi_3$ has the γ-$Ta(Pd,Rh)_3$-type structure, with a stacking of ten AB_3 layers in the sequence *ABCBCACBCB*. The space group is $P6_3/mmc$ (No. 194) and the unit-cell dimensions are $a = 5{\cdot}2822$ (2), $c = 21{\cdot}3916$ (18) Å at room temperature.

Introduction

Kirkpatrick & Larsen (1961) undertook an investigation of the Zr–Ni system and stated that the Hf–Ni system was analogous. In the region 65–80 at.% Ni they found two phases, Hf_2Ni_5 and Hf_2Ni_7, but no phase with the composition $HfNi_3$.

In a study of the entire Hf–Ni system, Svechnikov, Shurin & Dmitriyeva (1967) established the existence of three phases between 65 and 80 at.% Ni, namely Hf_2Ni_5, $HfNi_3$ and Hf_2Ni_7. $HfNi_3$ was said to possess the $TiNi_3$-type structure, but no unit-cell parameters were presented.

Bsenko (1978) investigated the Hf–Ni system in the region 65–80 at.% Ni by metallographic and X-ray methods. The existence of a phase with composition $HfNi_3$, forming peritectically from Hf_2Ni_7 and the melt, was confirmed. This high-temperature modification of $HfNi_3$ was found to be ductile, in contrast to the brittle modification obtained when the alloy is annealed at 1000 °C for 120 h. The purpose of this study was to determine the crystal structures of the two modifications of $HfNi_3$ by single-crystal X-ray diffraction.

Experimental

Two alloys with nominal compositions $Hf_{0{\cdot}25}Ni_{0{\cdot}75}$ and $Hf_{0{\cdot}26}Ni_{0{\cdot}74}$ were prepared by arc-melting turnings of Hf (containing 3% Zr, Koch-Light) and Ni (Specpure, Johnson Matthey & Co. Ltd) on a water-cooled Cu hearth under a purified Ar atmosphere. After the first melting the alloys were in the form of buttons, which were turned upside-down and remelted. The weight loss was less than 0·5%.

The alloy $Hf_{0{\cdot}25}Ni_{0{\cdot}75}$ was placed in a ZrO_2 crucible inside a silica tube. After evacuation the tube was sealed off and placed in a resistance furnace for 120 h at a temperature of 1000 °C. The tube was quenched in water and the specimen cut into two pieces. After one of the pieces had been polished and etched, a metallographic examination showed that the alloy was a single phase. The other sample was crushed and small fragments were examined on a Weissenberg camera. The symmetry indicated that the space group was $P6_3mc$, $P\bar{6}2c$ or $P6_3/mmc$. The alloy $Hf_{0{\cdot}26}Ni_{0{\cdot}74}$ was placed in a ZrO_2 crucible and heat treated for 24 h in a resistance furnace (Hereaus) at 1300 °C under very pure Ar gas. At this temperature the phase diagram shows that there is an equilibrium between the melt and the high-temperature α-$HfNi_3$. During the heat treatment the crystals of α-$HfNi_3$ grow larger. After the furnace had cooled, the specimen was cut, polished and etched, its surface showing large crystals of α-$HfNi_3$ surrounded by a fine eutectic. In order to isolate the ductile crystals, the sample was placed in a solution of *aqua regia*. The eutectic matrix dissolved after a few minutes and α-$HfNi_3$ crystals were isolated. They were washed and dried and Weissenberg photographs indicated that the space group was $R32$, $R3m$ or $R\bar{3}m$. X-ray powder photographs of α-HfNi$_3$ and the low-temperature β-HfNi$_3$ were taken using a Guinier–Hägg-type focusing camera (Philips XDC 700) with Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}54059$ Å), and zone-refined Si ($a = 5{\cdot}43088$ Å) as internal standard. Preliminary cell dimensions were obtained from the Weissenberg photographs and used to index the powder patterns. The unit-cell dimensions were refined using the local program *CELNE* (Ersson, 1976). A Nonius CAD-4F diffractometer controlled by a PDP8/A computer was used to record the intensities of the reflexions from the two phases. Graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) and the $\omega/2\theta$-scan technique were employed. During the data collection three reflexions were used as monitors and checked after every 50 reflexions. 933 independent reflexions up to 120° in 2θ were recorded for α-HfNi$_3$. For β-HfNi$_3$ the number of reflexions was 431 and the 2θ limit was 50°.

Structure refinements

F_o^2 and $\sigma(F_o^2)$ were obtained from the integrated intensities by applying corrections for background, Lorentz and polarization effects, and absorption.

The crystal of α-HfNi$_3$ was rather irregular. An approximation of the shape to a polyhedron bounded by 14 faces gave transmission factors varying from 0·04 to 0·14 ($\mu = 791$ cm^{-1}). The shape of the β-HfNi$_3$ crystal was a triangular prism and the absorption calculations gave transmission factors varying from 0·21 to 0·46.

The 009 and 0,0,18 reflexions from the α-HfNi$_3$ crystal and the 0,0,10 and 0,0,20 reflexions from the β-HfNi$_3$ crystal were very strong, indicating nine-layer and ten-layer types of structures respectively. The relationship between the c parameters for the two phases also supports this conclusion [$c(\alpha)/9 = c(\beta)/10$]. Triangular ordering within the layers is probable, since rectangular ordering would cause an orthorhombic distortion of the unit cells.

The rhombohedral symmetry and the nine-layer stacking for α-HfNi$_3$ made it probable that it was isostructural with BaPb$_3$ (Sands, Wood & Ramsey, 1964). A refinement was carried out in space group $R\bar{3}m$ with the atomic positions given for BaPb$_3$.

According to Beck (1967), a ten-layer structure with triangular ordering within the layers has 16 possible stacking sequences. The intensities for 25 reflexions were calculated for all 16 sequences and compared with those measured. After refinement of the scale factor, $R(F)$ values varying from 0·10 to 0·30 were obtained. For the five sequences that gave $R(F)$ values of 0·10, the intensities for all reflexions were calculated. Refinement of the scale factor yielded $R(F)$ values between 0·30 and 0·50 for four of these sequences, while the sequence *ABCBCACBCB* yielded a value of 0·18. This is the stacking sequence of γ-Ta(Pd,Rh)$_3$ determined by Giessen & Grant (1965). A refinement based on the positional parameters for this structure type was then carried out.

In the final refinement of the two structures, the full-matrix least-squares program *UPALS* (Lundgren, 1976) was used. The function minimized was $w(|F_o| - |F_c|)^2$, where the weights were applied according to $w^{-1} = \sigma^2(F_o) + (pF_o)^2$ and the empirical factor p was set at 0·03. One scale factor, three atomic positional parameters and four isotropic temperature factors were refined in the case of α-HfNi$_3$. The conventional agreement index $R(F) = \sum |F_o - F_c|/\sum |F_o|$ was 0·095 for 933 reflexions. In the case of β-HfNi$_3$, one scale factor, eight atomic positional parameters and six isotropic temperature factors were refined. The $R(F)$ value was 0·098 for 431 reflexions.

No refinements with anisotropic temperature factors were performed. Such a refinement would in this case be of little significance, since the strong absorption together with experimental errors in the geometrical description of the crystal influence the anisotropic temperature factors.

Atomic scattering factors for Hf and Ni were taken from Cromer & Waber (1965), and dispersion correction factors from Cromer & Liberman (1970). No extinction correction was performed.*

Discussion of the structures

The structures of α- and β-HfNi$_3$ can be described as stackings of close-packed layers parallel to (001) with triangular ordering within the layers. An example of such a layer is shown in Fig. 1. The stacking sequence of α-HfNi$_3$ is *ABABCBCAC* or, in the Jagodzinski

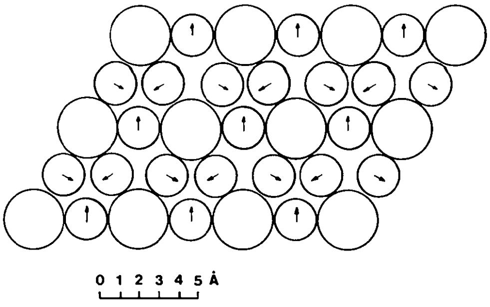

Fig. 1. A close-packed AB_3 layer with triangular ordering. The tendency of the small atoms to approach each other is indicated by arrows.

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* Lists of structure factors for both α and β forms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33756 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

notation, $(cch)_3$. If the structure were ideal, the stacking layers would be planar and equally spaced at a distance of $c/9$ Å, and the atoms in the close-packed layers would be situated on a net of equilateral triangles. In the structure of α-HfNi$_3$, the Hf(1) and Ni(1) atoms are situated on planar *c* layers while the Hf(2) and Ni(2) atoms are situated on puckered *h* layers. The Hf(2) and Ni(2) atoms are 0·07 and 0·02 Å, respectively, from the ideal *h* layer. Within the puckered *h* layers, the Ni(2) atoms are displaced from their ideal positions towards each other. This deviation from ideality can be explained by short-range repulsive interaction between nearest-neighbour atoms (Havinga, 1975). The positional and isotropic thermal parameters for α-HfNi$_3$ are given in Table 1.

β-HfNi$_3$ has the stacking sequence *ABCBCACBCB* or, in the Jagodzinski notation, $(hhchc)_2$. The planar layers in the structure consisting of Hf(1) and Ni(1) atoms are in positions of hexagonal close packing while the remaining Hf and Ni atoms are situated in puckered layers. The deviation from ideality is greatest for the *h* layers, where the Hf(3) and Ni(2) atoms deviate from the plane by 0·09 and 0·03 Å respectively. The *c* layers are less puckered, the deviation from planarity for the Hf(2) and Ni(3) atoms being 0·03 and 0·01 Å respectively. The tendency of the Ni atoms to approach each other within the layers is strongest in the *h* layers. Table 2 gives the positional and isotropic thermal parameters for β-HfNi$_3$.

Each atom in the two structures has a coordination number of 12. The atoms situated in a *c* layer have a cuboctahedral coordination figure, and the atoms in the *h* layers are twinned cuboctahedral. If the structures were ideal the interatomic distances would be equal, but because of the puckered layers and the tendency of the Ni atoms to approach each other, the coordination polyhedra are distorted. Interatomic distances for the two structures are given in Tables 3 and 4. Only distances less than 3·5 Å are included.

Table 1. *Final structural parameters for* α-HfNi$_3$

E.s.d.'s are in units of the least significant digit. Positional parameters are × 10^4, thermal × 10^2.

		x	*y*	*z*	*B* (Å^2)
Hf(1)	3(*a*)	0	0	0	53 (2)
Hf(2)	6(*c*)	0	0	2185 (1)	50 (1)
Ni(1)	9(*e*)	½	0	0	59 (3)
Ni(2)	18(*h*)	1780 (2)	3560 (5)	1099 (1)	57 (2)

Table 2. *Final structural parameters for* β-HfNi$_3$

E.s.d.'s are in units of the least significant digit. Positional parameters are × 10^4, thermal × 10^2.

		x	*y*	*z*	*B* (Å^2)
Hf(1)	2(*b*)	0	0	¼	42 (9)
Hf(2)	4(*f*)	⅓	⅔	3488 (2)	46 (7)
Hf(3)	4(*f*)	⅓	⅔	5458 (1)	56 (8)
Ni(1)	6(*h*)	5117 (9)	233 (2)	¼	54 (13)
Ni(2)	12(*k*)	1560 (5)	3119 (11)	514 (2)	71 (11)
Ni(3)	12(*k*)	8316 (6)	6633 (12)	1495 (2)	53 (10)

Table 3. *Interatomic distances* (Å) *less than* 3·5 Å *in* α-HfNi$_3$

E.s.d.'s are in units of the least significant digit.

Hf(1)—Ni(1) ×6	2·639 (1)	Ni(2)—Hf(1)	2·666 (1)
Ni(2) ×6	2·666 (1)	Hf(2) ×2	2·643 (1)
		Hf(2)	2·645 (1)
Hf(2)—Ni(1) ×3	2·683 (1)	Ni(1) ×2	2·579 (1)
Ni(2) ×6	2·643 (1)	Ni(2) ×2	2·466 (2)
Ni(2) ×3	2·645 (1)	Ni(2) ×2	2·605 (2)
		Ni(2) ×2	2·813 (2)
Ni(1)—Hf(1) ×2	2·639 (1)		
Hf(2) ×2	2·683 (1)		
Ni(1) ×4	2·639 (1)		
Ni(2) ×4	2·579 (1)		

Table 4. *Interatomic distances* (Å) *less than* 3·5 Å *in* β-HfNi$_3$

E.s.d.'s are in units of the least significant digit.

Hf(1)—Ni(1) ×6	2·643 (4)	Ni(2)—Hf(2)	2·682 (5)
Ni(3) ×6	2·644 (4)	Hf(3)	2·638 (5)
		Hf(3) ×2	2·646 (3)
Hf(2)—Ni(1) ×3	2·670 (2)	Ni(2) ×2	2·471 (8)
Ni(2) ×3	2·682 (5)	Ni(2) ×2	2·623 (8)
Ni(3) ×6	2·642 (3)	Ni(2) ×2	2·812 (8)
		Ni(3) ×2	2·571 (6)
Hf(3)—Ni(2) ×3	2·638 (5)		
Ni(2) ×6	2·646 (3)	Ni(3)—Hf(1)	2·644 (4)
Ni(3) ×3	2·684 (5)	Hf(2) ×2	2·642 (3)
		Hf(3)	2·684 (5)
Ni(1)—Hf(1) ×2	2·643 (4)	Ni(1) ×2	2·603 (5)
Hf(2) ×2	2·670 (2)	Ni(2) ×2	2·571 (6)
Ni(1) ×2	2·455 (1)	Ni(3) ×2	2·616 (8)
Ni(1) ×2	2·827 (1)	Ni(3) ×2	2·666 (8)
Ni(3) ×4	2·603 (5)		

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The Crystal Structure of Hf_8Ni_{21}

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The crystal structure of the intermetallic phase Hf_8Ni_{21} has been determined from single-crystal X-ray diffraction data. Hf_8Ni_{21} crystallizes in space group $P\bar{1}$ with $Z = 1$. The cell parameters are $a = 6{\cdot}4275$ (12), $b = 8{\cdot}0007$ (15), $c = 8{\cdot}5540$ (16) Å, $\alpha = 75{\cdot}18$ (1), $\beta = 68{\cdot}14$ (2) and $\gamma = 75{\cdot}61$ (2)°. A conventional $R(F)$ value of 0·11 was obtained for a full-matrix least-squares refinement, using 1440 independent reflexions. The coordination number for each Hf atom is 15, and for the 11 non-equivalent sets of Ni atoms it varies from 12 to 13. Hf_8Ni_{21} is a high-temperature phase, stable from 1300 ± 20 to 1175 ± 10°C, where it decomposes eutectoidally into Hf_3Ni_7 and $HfNi_3$ (low-temperature). The relationship between Hf_8Ni_{21} and Zr_2Ni_7 is discussed.

Introduction

Some observations on the Hf–Ni system were reported by Kirkpatrick & Larsen (1961). They stated that a phase of composition Hf_2Ni_5 existed, and from a comparison of the powder diffraction patterns for Hf_2Ni_5 and Zr_2Ni_5 they concluded that the two phases were isostructural. They tentatively indexed Zr_2Ni_5 on the basis of a pseudo-orthorhombic cell but the symmetry in their Weissenberg photographs appeared to be lower than orthorhombic.

Svechnikov, Shurin & Dmitriyeva (1967) found a phase of composition Hf_2Ni_5 which formed peritectically from the melt and $HfNi_3$, but gave no further characterization of this phase. In an investigation of the Hf–Ni system in the region 65–80 at.% Ni, Bsenko (1978*a*) found that the phase denoted Hf_2Ni_5 crystallizes with a triclinic unit cell and that the composition is Hf_8Ni_{21}. The investigation of the crystal structure of Hf_8Ni_{21} is presented in this paper.

Experimental

An alloy of nominal composition $Hf_{0{\cdot}28}Ni_{0{\cdot}72}$ was prepared by arc-melting Hf (containing 3% Zr, Koch-Light) and Ni (Specpure, Johnson Matthey & Co. Ltd) on a water-cooled Cu hearth. Before the alloy was melted, a getter alloy was melted for five minutes in order to remove oxygen and nitrogen from the protecting Ar atmosphere. The alloy was then placed in a ZrO_2 crucible and heat treated under very pure Ar gas in a resistance furnace for 24 h at 1275 °C. This heat treatment is necessary since, when the alloy solidifies in the arc-furnace, the crystals of Hf_8Ni_{21} formed are small and unsuitable for single-crystal X-ray work. During the heat treatment at 1275 °C the alloy partly melts and the small crystals of Hf_8Ni_{21} grow larger. After the heat treatment a metallographic examination of the specimen showed large crystals of Hf_8Ni_{21} surrounded by a fine eutectic consisting of Hf_3Ni_7 and Hf_7Ni_{10}. The sample was then placed in a solution of *aqua regia*, which dissolved the eutectic matrix leaving a batch of Hf_8Ni_{21} crystals. Attempts to obtain crystals of Hf_8Ni_{21} by crushing the sample resulted in severe crystal deformation owing to the great ductility of the phase. A suitable crystal was mounted on a Weissenberg camera and the diffraction symmetry showed the space group to be $P1$ or $P\bar{1}$.

A powder diffraction photograph was taken of a sample of small crystals of Hf_8Ni_{21}. A Guinier–Hägg camera (Philips XDC 700) with Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}54059$ Å) was used. Zone-refined Si ($a = 5{\cdot}43088$ Å) was used as internal standard. The powder pattern was