Electron diffraction study of the cobalt-rich Hf-Co intermetallic compounds

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ABSTRACT

Intermetallic compounds in a range of compositions from HfCo_4 to HfCo_8 were investigated by transmission electron microscopy, selected-area electron diffraction, and energy-dispersive x-ray spectroscopy. A major crystalline phase, closely related to the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase in structure, has been observed in all the samples from HfCo_6 to HfCo_8 . The phase, referred to as either $\text{Hf}_2\text{Co}_{11}$ or HfCo_7 phase in the literature, are suggested to belong to a common phase, having a broad composition range and referred to as μ -phase in the present paper. The coexistence of the μ -phase, FCC Co and a minor Hf_2Co_7 phase was observed. The $\text{Hf}_6\text{Co}_{23}$ phase has been identified in the samples of HfCo_4 and HfCo_5 . Tilt-series electron diffraction study reveals that the μ -phase is a 1-dimensional incommensurate modulated structure, which can be described approximately as B-center orthorhombic with $a = 0.47$ nm, $b = 0.82$ nm, $c = 3.86$ nm.

Keywords

Hf-Co; Electron Diffraction; Crystal Structure; Intermetallic Compound; Magnetic Materials

1. Introduction

The recent push toward renewable energy and green technology has created a surge in the demand for permanent magnets. However, the highest energy product magnets require rare-earth elements such as samarium and neodymium. Additionally, there is a large gap in the maximum energy product between alloys that contain rare-earth elements and those that do not. New rare-earth-free magnetic materials with high energy products are urgently needed. The studies from various research groups show that a Co-rich Hf-Co intermetallic compound with non-cubic high anisotropy structure is a potential permanent magnet candidate due to its high Curie temperature. Early research on the magnetic properties in the Hf-Co system was carried out about 35 years ago [e.g., 1,2]. Recent investigations focus on the improvement of the magnetic behavior on melt-spun ribbons and nano-particles with the additions of third elements [3-6].

McGuire *et al.* [3] reported the hard ferromagnetic behavior for a crystalline phase in $\text{Hf}_2\text{Co}_{11}\text{B}$ produced by melt-spinning. Das *et al.* [4] reported the structural and magnetic properties of melt-spun HfCo_7 and HfCo_7 -based alloys. A model crystal structure for HfCo_7 has been proposed to estimate the magnetic properties. Balamurugan *et al.* [5] investigated the structural and magnetic properties of nanostructured Co-rich transition metal alloys, $\text{TM}_x\text{Co}_{100-x}$ (TM = Hf, Zr and $10 \leq x \leq 18$). The formation of high anisotropy HfCo_7 and $\text{Zr}_2\text{Co}_{11}$ phases was found in a relative broad composition region. Chang *et al.* [6] reported that hard magnetic property enhancement was achieved in melt spun $\text{Hf}_{12}\text{Co}_{88}$ ($\approx \text{HfCo}_{7.3}$) ribbons with boron as doping element.

Compositions and crystal lattices of the Co-rich non-cubic Hf-Co phase reported in the literature are inconsistent, which could be the reason that both $\text{Hf}_2\text{Co}_{11}$ and HfCo_7 have been used for Hf-Co magnetic materials. In this paper, we argue that the two intermetallic compounds actually are a common crystalline phase with a range of compositions that we refer to as μ -phase. The Hf_2Co_7 , $\text{Hf}_6\text{Co}_{23}$ and HfCo_7 phases are listed in the well-used phase diagram [7,8]. The first reliable lattice parameters of the HfCo_7 phase were reported by Demczyk and Cheng [9]. In this work, selected-area electron diffraction (SAED) patterns from the orthorhombic HfCo_7 and $\text{Zr}_2\text{Co}_{11}$ compounds were found to be similar for the three main zone axes. More detailed transmission electron microscopy (TEM), high-resolution electron microscopy (HREM) and SAED studies on the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase were reported by Ivanova *et al.* [10] and Li *et al.* [11]. Although they used HfCo_7 to represent the phase, Demczyk and Cheng [9] pointed out the actual composition of the compound was probably closer to HfCo_6 rather than HfCo_7 . In the tentative Hf-Co phase diagram proposed by Dwight and Nevitt [12], the Hf-Co phase with the highest Co content is HfCo_6 . In the most recent work by Lu *et al.* [13], $\text{Hf}_2\text{Co}_{11}$ instead of HfCo_7 was identified as a stoichiometric phase and no observation of the Hf_2Co_7 phase was reported. Needless to say, the composition and structure of the Co-rich Hf-Co compounds needs to be further clarified and studied.

In the present work, the Co-rich Hf-Co compounds have been investigated by TEM, SAED and energy-dispersive x-ray spectroscopy (EDS) techniques. Especially, the structure of the orthorhombic Hf-Co phase were systematically studied tilt series of SAED experiments. The current structural models of the orthorhombic Hf-Co phase were checked and the structural relationship of the orthorhombic Hf-Co phase to the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase was discussed.

2. Experimental procedures

Ingots in a range of nominal compositions from HfCo_4 to HfCo_8 were arc melted from high-purity elements (99.9% Hf and 99.995% Co from Alfa Aesar) in an argon atmosphere. The ribbons about 2 mm wide and 50 μm thick were made by ejecting molten alloys in a quartz tube onto the surface of a copper wheel in room temperature at tangential wheel speeds of 20, 30 and 40 m/s. The ribbons were selected for TEM and SAED experiments and the magnetic property measurements.

The ribbons usually contain nano-sized crystalline grains due to the rapid quenching process. Heat treatment is required to increase crystalline grains for carrying out the tilt series of SAED experiment conveniently. Selected ribbons were sealed in a quartz tube with high purity of argon and annealed at 1140 $^{\circ}\text{C}$ for 48 hrs and then quenched in ice water. TEM samples were made from both original and annealed ribbons cutting into pieces approximately 2 mm long and mechanically ground and polished to approximately 30 μm or thinner; following mounting onto 3 mm diameter Cu or Mo rings, the samples were further ion-beam (Ar^+) milled (4kV, start at 10 $^{\circ}$ and then decrease to 6 $^{\circ}$, Gatan PIPS II) to electron transparency.

TEM and SAED experiments were carried out on JEOL JEM2010 and FEI Tecnai Osiris microscopes equipped with Gatan Erlangshen and Orius CCD cameras, respectively. Both of them are operating at 200 kV and equipped with a double-tilt stage and an EDS detector. Crystalline phases were first examined by EDS analysis, followed by bright-field (BF) and dark-field (DF) TEM imaging and tilt series of SAED works. EDS data were collected with the

ChemiSTEM system on FEI Tecnai Osiris microscope and analyzed with the Bruker Esprit software. The experimental SAED patterns were analyzed using JEC/SP [14], SAED2 [15] and JEC/QSAED [16] software. JEC/SP is software for generating stereographic projections, applicable to specimen orientation adjustment in TEM experiments. SAED2 is software for simulation and analysis of electron diffraction patterns. JEC/QSAED is software for quantification of crystalline SAED patterns.

3. Results and discussion

For reader's convenience, three Co-rich Hf-Co compounds, *viz.*, Hf₂Co₇, Hf₆Co₂₃ and HfCo₇, in the Hf-Co phase diagram [7,8] are listed in Table 1, together with the results in the work by Das *et al.* [4], Shah [17] and the present work.

3.1. TEM study of the Co-rich Hf-Co compounds

Fig. 1 shows a TEM image of the annealed ribbon with the nominal composition HfCo₆. Most grains were identified as the Co-rich orthorhombic Hf-Co phase. Fine strips can be observed in some of the grains in suitable orientations. Fig. 2 shows the EDS spectrum collected on one of the grains of the Co-rich orthorhombic Hf-Co phase, the Esprit standardless analysis shows Hf_{14.1}Co_{85.9} and the standard deviation is within $\pm 10\%$. The grains of the Co-rich orthorhombic Hf-Co phase are accompanied by the FCC Co phase with the light-grey contrast. The Hf₂Co₇ phase was also observed occasionally in adjacent areas. Similar morphologies were also observed in the ribbons in a range of nominal compositions from HfCo₆ to HfCo₈. Fig. 3

shows (a) BF and (b) DF TEM images of a sample with the nominal composition HfCo_7 . The most bright diffraction spot was chosen for the condition for DF imaging. The Co-rich orthorhombic Hf-Co phase, the FCC Co phase and the Hf_2Co_7 phase are marked in the BF and DF images. A detail SAED study of the orthorhombic phase is presented in section 3.2. Fig. 4 shows the SAED patterns of (a) the FCC Co phase along [001] zone axis and (b) the Hf_2Co_7 phase along [001] zone axis. Fig. 5 shows a TEM image of a ribbon with the nominal composition HfCo_4 , which reveals a different morphology compared to those in Figs. 1 and 3. The SAED and EDS experiments identified the crystalline grains to be the cubic $\text{Hf}_6\text{Co}_{23}$ phase. The experimental and calculated SAED patterns of the cubic $\text{Hf}_6\text{Co}_{23}$ phase along [001] zone axis are shown in Fig. 6.

The present work confirms the existence of the three Co-rich Hf-Co intermetallic compounds, *viz.*, Hf_2Co_7 , $\text{Hf}_6\text{Co}_{23}$ and $\mu\text{-HfCo}$, a Co-rich orthorhombic Hf-Co phase with the composition between $\text{Hf}_2\text{Co}_{11}$ and HfCo_7 . The $\mu\text{-HfCo}$ is used to here to avoid the nomination of the intermetallic compound to the stoichiometric composition of $\text{Hf}_2\text{Co}_{11}$ or HfCo_7 . The composition of the same compound was found to be $\text{Hf}_2\text{Co}_{11}$ [3, 13], HfCo_6 [9, 12] and HfCo_7 [5-8], which indicates that the compound exists in a range of composition. A possible interpretation is that some atomic positions in the μ -phase may be occupied by either Hf or Co, and the possibility of vacancies in some atom positions.

3.2. SAED study of the μ -phase

SAED patterns of the μ -phase are given in Fig. 7 (a), which were selected from multiple experiments and arranged together from [010] to [100] and from [100] to [001] zone axes with the help of the JECF/SP software. The tilting angles were determined in tilt series of experiments and the zone axes were calculated using the orthorhombic lattice parameters in the present work. It is noticeable that the SAED patterns along [110], [501] and [14 0 1] are similar to those along the main zone axes, i.e., [010], [100] and [001], respectively. The existence of the similar SAED pattern pair reflects the structural features of the μ -phase, (a) the angle between the [010] and [110] axes is near 30° ; (b) the angle between the [100] and [501] axes is near 60° ; (c) the angle between the [001] and [14 0 1] axes is near 60° . According to the symmetrical relation, the first pair imply the $[-1\ 1\ 0]$ zone axis is on the other side of the $[0\ 1\ 0]$ zone axis with an angle near 30° . Therefore the angle between the $[1\ 1\ 0]$ and $[-1\ 1\ 0]$ zone axes is near 60° . The last two pairs can be understood in consideration of the pseudo-sixfold symmetry of the strong diffraction spots in the SAED pattern of the [010] zone axis.

The SAED patterns of the three main zone axes were firstly reported by Demczyk and Cheng [9]. Unfortunately, a similar SAED pattern of the [100] pattern in Fig. 7(a) was misinterpreted as a composite pattern comprised of [100] and $[h0l]$ zone axes. For most crystal phases, the same chain of the diffraction spots $(00l)$, $l = \pm 1, 2, 3, \dots$, can always be observed correspondingly in the SAED patterns along the [100] and [010] zone axes. However, it is not so obvious for the μ -HfCo phase, which may cause this confusion. In order to reveal the correspondence of the $(00l)$, $l = \pm 1, 2, 3, \dots$, in the SAED patterns along the [100] and [010] zone axes, Fig. 7(b) shows an enlarged [100] SAED pattern of the μ -HfCo phase and Fig. 7(c) one with a slight tilting away about 1.2° of the exact [100] zone axis. It is clear that more diffraction

spots in Fig. 7(c) reveal the extinct diffraction spots in Fig. 7(b). Thus the corresponding relationship between the diffraction spots in the SAED patterns along the [100] and [010] zone axes is restored for the μ -HfCo phase.

Fig. 8(a) shows an enlarged SAED pattern of the μ -HfCo phase along the [010] zone axis, with strong diffraction spots marked with arrows to indicate a pseudo-hexagonal symmetry. In order to elaborate the feature of the modulation along the c axis, the distribution of diffraction spots was analyzed using JECF/QSAED. An intensity profile mapping to the intensity distribution along the near column is shown in the inset. In Fig. 8(b) some of reflections land on the periodic spacing marks while the others mismatch to the periodicity. This means that the periodicity exists locally but is lost in the whole pattern. The diffraction pattern of a modulated structure can be indexed using more than three indices as follows [18]:

$$\mathbf{Q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}^*$$

$$\mathbf{q}^* = q_1\mathbf{a}^* + q_2\mathbf{b}^* + q_3\mathbf{c}^*$$

For the μ -HfCo phase, $q_1 = 0$, $q_2 = 0$, $q_3 = 0.07$. The basic lattice is a pseudo hexagonal lattice, which can be described as a base-centered orthorhombic lattice with $a = 0.47$ nm, $b = 0.82$ nm and $c = 0.27$ nm. Similar to the structure of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase [11], the structure of the incommensurate modulated μ -HfCo phase can be approximately described as a B-centered orthorhombic lattice with $a = 0.47$ nm, $b = 0.82$ nm and $c = 3.86$ nm. For this reason, the incommensurate modulated μ -HfCo phase was also called an orthorhombic phase in the present work.

3.3. Twin structure of the μ -phase

The TEM image in Fig. 9(a) shows a twin boundary of the μ -HfCo phase. Contrast variance was noted along the nearly straight twin boundary in grain 2. Twinned SAED patterns in Fig. 9(b) were taken from both of grains 1 and 2 along the [010] zone axis. A simulated electron diffraction pattern in Fig. 9(c) was calculated based upon a one-atom-motif B centered periodic approximant. The simulation reproduces the geometrical features of the strong diffraction spots in the experimental pattern; one example is marked with circles in Figs. 9(b) and 9(c). The positions of the weak diffraction spots were not expected to match each other due to the over-simplified model, and neither were the diffraction intensities.

Since the μ -HfCo phase is similar to the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase in structure, the twin mechanism of the two compounds is considered to be the same. The HREM images of the twinned grains of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase show a coherent twin boundary in a zigzag pack of hexagonal atomic clusters, which can be viewed approximately as a straight line at lower magnification. The formation of a twinned interface can be interpreted as the twinned grains sharing the common hexagonal structural motifs [11].

Besides the SAED patterns of twinned grains along the [010] zone axis (a top view), the twinned relationship of the μ -HfCo phase was also observed in a side view. Fig. 10 shows (a) a twin boundary of the μ -HfCo phase, (b) an SAED pattern along [100] zone axis taken from grain 1 and (c) an SAED pattern along [501] zone axis taken from grain 2. Although a pair of the

SAED patterns similar to Figs. 10(b) and (c) were reported by Demczyk and Cheng [9], the twinning relationship between the two patterns has been established for the first time in the present work.

3.4. Current models of the μ -HfCo phase

An atomic hardcore model was constructed as an approximate description of the HfCo₇ structure, in which two formula units in the unit cell were suggested according to the metallic radii of dense-packed Hf and Co atoms [4, 17]. The lattice parameters, space group of the model are listed in Table 1 and the atom coordinates of the model are listed in Table 2. Fig. 11 shows the simulated XRD pattern based on the model and the updated lattice parameters [17]. It shows that the three strongest peaks fit to the experimental XRD pattern (Fig. 1 in reference [4]). The model is used to interpret the magnetization and the magnetic anisotropy. The same model was lately quoted and used to interpret the experimental results of HfCo₇ doped with Si by Chang *et al.* [6]. In order to evaluate this model, the simulation of the SAED patterns was carried out. Fig. 12 shows the structural projections of this model along (a) [001], (b) [010], and (c) [100] zone axes and the calculated SAED patterns are along (d) [001], (e) [010], and (f) [100] zone axes, respectively. Unfortunately this model is not supported by the experimental SAED patterns of the μ -HfCo phase as shown in the simulation.

Nguyen *et al.* [19] applied an adaptive genetic algorithm to search for low-energy structures of the Hf-Co system. For 16 atoms per unit cell, the lowest energy structure is a monoclinic, $a = 0.4623$ nm, $b = 0.8088$ nm, $c = 1.051$ nm, $\beta = 80.76^\circ$. For 32 atoms per unit cell,

the lowest energy structure is monoclinic, $a = 0.4523$ nm, $b = 1.1820$ nm, $c = 1.145$ nm, $\beta = 92.77^\circ$. It is worthy of noticing that both of the two structural models contains the SmCo_5 structural motif. Similar local structure was also derived for low-energy structures of the Zr-Co system with the adaptive genetic algorithm [19]. Although the lattice types and parameters do not match with the experimental result in the present work, the local atomic cluster might be useful for the structural investigation of the $\mu\text{-HfCo}$ phase in view of the successful modeling for the rhombohedral $\text{Zr}_2\text{Co}_{11}$ phase [20].

Our work on a new model is underway in the combination of the local structure deduced from the adaptive genetic algorithm, the HREM images and the SAED patterns and XRD diagrams of the $\mu\text{-HfCo}$ phase and the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phases. The results will be published separately.

3.5. Discussion

As mention above, the $\mu\text{-HfCo}$ phase in the present paper refers to the intermetallic phase HfCo_7 (and $\text{Hf}_2\text{Co}_{11}$) in literature. Buschow *et al.* [1] first reported the phase with a composition of HfCo_7 with a tetragonal crystal structure with, $a = 0.707$ nm and $c = 0.78$ nm. Later, one of these authors [2] reported the phase in a composition of HfCo_7 to be hexagonal with $a = 0.5477$ and $c = 0.807$ nm. The present work shows that the lattice parameters favor the result reported by Demczyk and Cheng [9], except the primitive orthorhombic lattice is replaced by a base-centered orthorhombic lattice in the present work.

Most work so far on the structural characterization and the phase identification of the μ -HfCo phase were based on XRD techniques. Some structural features of the μ -HfCo phase might prove difficult using only XRD, including (a) the heavily overlapped diffraction peaks due to the large lattice parameters; (b) the possible coexistence of a minor phase, *e.g.* FCC Co and Hf₂Co₇; and (c) a 1-dimensional incommensurate modulated structure. It should note that a solution may be obtained indexes the XRD spectra but may not be the true lattice. An XRD study of melt-spun HfCo₇ ribbons by Das *et al.* [4] was analyzed by TOPAS (Total Pattern Analysis Solution, Bruker AXS) and the updated lattice parameters were given by Shah [17]. Table 3 shows how the lattice parameters are related to the result in the present work. It is suggested that the electron diffraction analysis is suitable to determine the lattice from tilt series, as shown in this case. On the other hand, the electron diffraction analysis does not provide the precision that is available using XRD. The advantage of the XRD analysis can provide very precise data with the help of computer software such as TOPAS. The combination of the electron diffraction and XRD analysis will achieve the best results.

4. Conclusions

In summary, the investigation of the Co-rich Hf-Co alloy by using transmission electron microscopy and electron diffraction shows the existence of a 1-dimensional incommensurate modulated μ -HfCo phase as a major phase, together with FCC Co and the Hf₂Co₇ phases. The μ -HfCo phase, similar to the orthorhombic Zr₂Co₁₁ phase in structure, can be viewed approximately as a B-centered orthorhombic lattice with lattice parameters listed in Table 1. This

work reveals the main characteristic structural features of the μ -HfCo phase, whose detailed atomic structure still poses a challenge to future experimental research.

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Figure Caption

Figure 1. TEM image of a sample with the nominal composition HfCo_6 . Grains of the $\mu\text{-HfCo}$, the FCC Co phase, and the Hf_2Co_7 phase are marked. Fine strips can be observed in some grains of the $\mu\text{-HfCo}$, the directions of two groups of fine strips are marked with arrows.

Figure 2. EDS spectrum on one of the grains of the Co-rich orthorhombic $\mu\text{-HfCo}$ phase. The analysis show the composition of the phase is near to HfCo_6 .

Figure 3. (a) BF and (b) DF TEM images of a sample with the nominal composition HfCo_7 . Grains of the $\mu\text{-HfCo}$, the FCC Co phase, and the Hf_2Co_7 phase were marked. Fine strips can be observed in some grains of the $\mu\text{-HfCo}$.

Figure 4. SAED patterns of (a) the FCC Co phase along the $[001]$ zone axis and (b) the Hf_2Co_7 phase along the $[001]$ zone axis.

Figure 5. TEM image of the cubic $\text{Hf}_6\text{Co}_{23}$ phase in a sample with the nominal composition HfCo_4 .

Figure 6. (a) Experimental and (b) simulated SAED pattern of the cubic $\text{Hf}_6\text{Co}_{23}$ phase along the $[001]$ zone axis.

Figure 7. (a) SAED patterns of the μ -HfCo from the [010] to the [100] and from the [100] to the [001] zone axes. (b) An enlarged SAED pattern along the [010] zone axis and (c) the same SAED pattern after tilting away about 1.2° from the zone axis.

Figure 8. (a) An enlarged SAED pattern of the μ -HfCo along the [010] zone axis and (b) the distribution of the diffraction spots along the adjacent line. Pseudo sixfold symmetry is outlined with arrows. The distribution of the diffraction spots mismatches with the periodic grids, which reveals the incommensurate modulated structure.

Figure 9. (a) TEM image of the twinned μ -HfCo along the [010] axis (top view), (b) twinned SAED pattern and (c) simulation of the μ -HfCo. Geometrical features of the strong diffraction spots can be viewed in the experimental and simulated patterns, one example is marked with circles in Figs. 9(b) and 9(c).

Figure 10. (a) TEM image of the twinned μ -HfCo (side view), twinned SAED patterns of (b) along the [100] zone axis in the grain 1 and (c) along the [501] zone axis in the grain 2.

Figure 11. Simulated XRD pattern based on the model [4] and the updated lattice parameters [17]. Lattice parameters and atom coordinates are listed in Tables 1 and 2. The three strongest peaks in the simulated XRD pattern fit to the experimental XRD pattern (Figure 1 in reference [4]).

Figure 12. Structural projections of a model of an orthorhombic HfCo₇ phase in [4] along (a) the [001] (b) the [010] (c) the [100] zone axes; the simulated ED patterns along (d) the [001] (e) the [010] (f) the [100] zone axes, respectively. Hf atom in bigger radius is shown in golden color and Co atom is shown in light blue (colors only in web version).

Table 1. Crystalline structures of Co-rich Hf-Co intermetallic compounds.

Phase	Crystalline lattice (nm)	Type	Reference
HfCo ₇	Pcna, $a = 0.47$, $b = 0.83$, $c = 3.8$	Orthorhombic	Demczyk and Cheng [9]
HfCo ₇	Pmmm, $a = 0.4719$, $b = 0.4278$, $c = 0.8070$	Orthorhombic	Das <i>et al.</i> [4]
HfCo ₇	Pmmm, $a = 0.5498$, $b = 0.4714$, $c = 0.8054$	Orthorhombic	Shah [17]
μ -HfCo	B-centred, $a = 0.47$, $b = 0.82$, $c = (3.86)^\dagger$	Orthorhombic	The present work
Hf ₆ C ₂₃	Fm-3m, $a = 1.1502$	Th ₆ Mn ₂₃	Buschow <i>et al.</i> [1]
Hf ₂ Co ₇	C2/m, $a = 0.4444$, $b = 0.8191$, $c = 1.214$	Zr ₂ N ₁₇	Buschow <i>et al.</i> [1]

[†] It is incommensurate along the c axis and the 3.86 nm is an averaged lattice parameter.

Table 2. The atom coordinates of the HfCo₇ model by Das *et al.* [4] and the lattice parameters and space group of the model by Das *et al.* [4] and Shah [17] are listed in Table 1. The lattice parameters in Shah [17] should be used with the model.

atom	x	y	z	occupation
Co	0.0	0.5	0.0	1.0
Co	0.25	0.0	0.0	1.0
Co	0.0	0.0	0.25	1.0
Co	0.5	0.0	0.25	1.0
Co	0.25	0.5	0.25	1.0
Co	0.5	0.5	0.5	1.0
Co	0.3	0.0	0.5	1.0
Hf	0.5	0.5	0.0	1.0
Hf	0.0	0.5	0.5	1.0

Table 3. Comparison of the lattice parameters of the Co-rich orthorhombic HfCo phase.

Lattice Parameters	Type	a (nm)	b (nm)	c (nm)
Das <i>et al.</i> [4]	Orthorhombic (P)	0.4719	0.8070	0.4278

Shah [17]	Orthorhombic (P)	0.4714	0.8054	0.5498
Present work	Orthorhombic (B)	0.47	0.82	(3.86) [†]

For comparison, the a , b and c axes in Das *et al.* [4] and Shah [17] were exchanged in this Table.

[†] $3.86/0.4278 = 9.023 \approx 9$ and $3.86/0.5498 = 7.021 \approx 7$

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Graphical Abstract