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TEM STUDY OF THE REACTION MECHANISMS INVOLVED IN THE CARBOTHERMAL REDUCTION OF HAFNIA

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Keywords:

hafnium oxycarbide, TEM, carbothermal synthesis, reaction mechanisms, phase transformation

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Abstract:

The synthesis of HfC_xO_y oxycarbides through carbothermal reaction of hafnia with carbon black was undertaken. The obtained powders at different rates of advancement were studied by TEM and XRD in order to investigate the reaction mechanisms involved during such a transformation. The contact between the two starting reactants is shown to be non-reactive attesting that the transformation operates through solid-gas reactions. The hafnia phase is destabilized by the $\text{CO}_{(\text{g})}$ rich atmosphere and is consumed by the migration of ledges at the surface of the crystals acting as a zipper mechanism that liberates $\text{HfO}_{(\text{g})}$ and $\text{CO}_{2(\text{g})}$ species. The carbon dioxide thus released is used in return to oxidize the carbon black forming carbon monoxide through the Boudouard equilibrium. The liberated $\text{HfO}_{(\text{g})}$ then reacts with the ambient $\text{CO}_{(\text{g})}$ to form the oxycarbide phase which is shown to nucleate in the carbon black areas. Oxycarbide nuclei display a core shell microstructure which is formed by a single crystal core embedded in an oxygen rich amorphous phase. During the final stage of the reaction, the atmosphere saturated in $\text{CO}_{(\text{g})}$ progressively reduces the oxygen rich gangue that finally disappears. The accurate determination of the cell parameter of the oxycarbide phase during the reaction indicates that the first formed compound is nearly saturated in carbon compared to the metallic carbide. The tiny evolution of the lattice parameter indicates that the chemical composition is very restricted so that the solid solution of oxygen within the hafnium oxycarbide seems to be very limited.

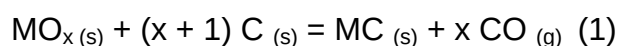
Introduction

Zirconium, titanium and hafnium carbides (IV Group transition-metal carbides) own a mix of properties which allow classifying them as UltraHigh Temperature Ceramics (UHTC) (high hardness, high electrical conductivity, high melting point, highly corrosion resistance and a good wear resistance) [1-3]. These performances predestine them to be used as thermal barriers in the aerospace, as materials for solar energy exploitation, as melting pot or as wear resistant coating [1-4]. Similar to the IV group transition-metal, the hafnium carbide (HfC_x) presents a rocksalt type structure well known for its nonstoichiometric behavior due to the occurrence of variable amount of carbon vacancies on the octahedral site ($0.50-0.59 < x < 0.98-1$) [5, 6].

Several synthesis ways were developed to produce carbide coatings : reactive magnetron sputtering [7], low-pressure chemical vapor deposition (LPCVD) [8] and carbide powders by mechanosynthesis [9, 10]. These last years, non-conventional routes were developed in order to obtain HfC powders whose size grading is fine. *Sacks et al.* [11] used a mixture of metal alkoxide and carbon sources (phenolic resin or glycerol) to obtain powders which were subsequently pyrolysed. A heat treatment in the range of 1200-1800°C under flowing argon allows producing carbides. The final material is shown to be sub-stoichiometric and some oxygen is found, substituted to carbon, forming an oxycarbide compound with HfC_xO_y formulae. At 1475°C, the crystallite size (~ 50 nm) was determined from XRD spectra using the Scherrer Equation. More recently, 100-200 nm grain size carbides (pure at $\sim 97\%$) were obtained by pyrolysing HfCl_4 and citric acid monohydrate [12] at 1600°C and near-stoichiometric carbides with sub-micron grain size were fabricated [13] by using an method of electro-deoxidation of hafnium dioxide (HfO_2) and graphite powder.

However, these methods are generally used to produce limited quantities of carbides. In this context the most common way to synthesize carbide powders at the industrial scale is the carbothermal reduction, this process being well suited to produce large amounts of powders with a good reproducibility. Many authors have undertaken kinetics and thermodynamics studies on the carbothermal reduction of zirconia (ZrO_2) [14-17] and titanium dioxide (TiO_2) [18, 19], but the Hf-C system has been much less studied. In particular, the carbothermal reduction of hafnia (HfO_2) by carbon black has never been investigated by a structural approach and particularly by transmission electron microscopy (TEM). However, with a melting point near 3950°C , the hafnium carbide (HfC_x) is one of the most refractory materials. In addition, it is interesting to note that the hafnium carbide can form a substitution solid solution with zirconium carbide [20]. Indeed, on the one hand hafnia is an isotype form of ZrO_2 which is often present as an impurity in zirconia powders samples and on the other hand HfO_2 - ZrO_2 dioxides powders can be mixed up to get oxycarbides showing intermediate composition together with associated melting temperatures.

The carbothermal reduction consists in the reaction of a metal oxide powder and carbon (carbon black or graphite) to form a carbide phase with the release of carbon monoxide following:



Zhelankin *et al.* [21] first put emphasis on the increase of the unit cell parameter of the non-stoichiometric HfC_x hafnium carbides with the increase of carbon amount (x). It is however now well admitted that in the case of carbothermal reactions an oxycarbide phase showing HfC_xO_y formulae is formed, at least before the evolution towards the final stoichiometric carbide [11, 13, 22]. The linear correlation relevant to the Vegard law between the lattice parameter and the composition of the oxycarbide

phase was established by Constant *et al.* [23]. Finally, the formation of an intermediate monoclinic oxycarbide was suggested by Liu *et al.* [22] but this fact was never confirmed by other authors that better suggested a cubic structure.

This contribution presents the results of the first structural and microstructural study carried out by coupling TEM and XRD in order to investigate the reaction mechanisms involved during the carbothermal transformation of hafnia. The results so obtained will be discussed under the light of the results obtained on this system by other authors. In addition, they will also be compared to those obtained in a previous study dedicated to the TEM study of the reaction mechanisms involved in the carbothermal reduction of zirconia that can be considered as a very close chemical system [24].

2) Experimental procedure: synthesis protocol of the oxycarbide powders and characterization

In order to get comparable results with previous TEM studies devoted to the carbothermal reduction of zirconia [24] and rutile [25], the same carbon black was used for the carbothermal reduction of the hafnia powders (commercial amorphous carbon black, 99.25 at.%, Prolabo, France). However, as in the literature several studies have highlighted the influence of the initial grain size of the dioxide on the size of the obtained oxycarbide grains, we choose hafnia powders showing nanometer-sized crystals. These starting powders, provided by the Centre de Transfert des Technologies Céramiques (CTTC) of Limoges (France) required a former heat treatment under air at 600°C for 4 h (Vectar furnace, Chesterfield, United Kingdom) in order to eliminate some chlorine impurities (Cl = 0.90 at.%). After treatment, the purity is close to 99.9% including a restricted amount of zirconia

impurities ($\text{Zr} < 0.5 \text{ at.}\%$). For the synthesis of the oxycarbide phase, the starting reactants have been weighted in fixed proportions fitting the theoretical equation (1). They were then mixed in a low speed planetary ball mill (Pulverisette 6, Fritsch) using ten balls (100% tungsten carbide) with a diameter of 1.0 mm. The blending sequence was composed of 5 pulses of 1 min at 200 rpm interrupted by pauses of 5 min to avoid heating. Then, the mixture was treated in a graphite furnace (AET Technologies, Rambouillet, France) under flowing argon (30 L/h).

In order to understand the mechanisms involved in the carbothermal reduction of hafnia, it is necessary to observe samples selected at different steps of the reactional process. The advancement (named ξ) can be controlled by measuring the weight loss of the sample. This reaction rate has been determined as the “experimental weight loss” over “theoretical weight loss” ratio. The theoretical weight loss is 22.72 % for the chosen stoichiometry. The different advancements obtained by varying the heating treatments, *i.e* the dwelling time and the temperature, are reported in Table 1.

The crystallized phases in the oxycarbide samples were identified by X-Ray diffraction (D5000, Siemens AG, Munich, Germany) for angle (2θ) ranging between 10° and 125° (step: 0.020° , step time: 1.6 s) using the $\text{Cu K}\alpha_1$ - $\text{K}\alpha_2$ radiations. A second diffractometer was used to determine the lattice parameters of the oxycarbide phase (D8 Advance Bruker, Karlsruhe, Germany) equipped with a front Johansson germanium monochromator which allows selecting the $\text{Cu K}\alpha_1$ radiation. The lattice parameters were refined by the method of Le Bail using the Fullprof® software [26]. This kind of refinement implies the knowledge of the space group of each crystallized phases present in the sample. However, this method does not require the knowledge of the atomic positions. It is generally used to determine new structures and allows

predicting the symmetry comparing profiles fits of different space groups [27] and is then well appropriated for accurate determinations of lattice parameters. Beforehand, for a quantitative exploitation of the XRD data, in particular to get reliable values of cell parameter measurements, an internal standard (Al_2O_3 Corundum) was mixed with a ratio of 50 wt.% to the synthesized oxycarbide powders in order to correct the sample position.

Transmission electron microscopy (TEM) characterizations were performed with a JEOL 2010 and a TEM-STEM JEOL 2100 microscope (JEOL, Tokyo, Japan) operating at 200 kV. TEM samples were elaborated by crushing powders in an agate mortar with water. A small drop containing some grains has been deposited on a copper grid covered by holey carbon film.

3. Results

3.1 *The starting reactants: $\xi=0$*

The starting hafnia powder is crystallized under its monoclinic form (JCPDS file n° 00-043-1017) as shown by the X-ray diffraction pattern provided in Figure 1a. The hafnia grain size, supposed spherical, was determined using the Fullprof® software. The contribution of the instrumental resolution function (IRF) was determined by a previous study performed with a perfectly crystallized lanthanum hexaboride standard (LaB_6). The contribution of the Gaussian function approached to a zero value and the determination of the integral width of the Lorentzian part allowed us to measure a hafnia grain size of $\sim 17 \text{ nm} \pm 1 \text{ nm}$. The laser granulometry experiences show a bimodal distribution of grain size centered on values of 20 nm and 170 nm. The TEM study confirms that the hafnia powder is made up of two distinct populations. The elementary particles corresponding to crystallites show a diameter of 15-20 nm which

is very similar to that measured by XRD (Figure 1b). The selected area electron diffraction (SAED) pattern (insert in Figure 1 b) presents quite continuous diffraction ring in agreement with the grain size observed and confirms the monoclinic cell (Space Group $P2_1/c$) as shown by the occurrence of the (100) first tenuous rings. It also reveals that the elementary crystallites are strongly gathered forming ball shaped aggregates (see circled regions in Figure 1c) which size does not exceed 100-200 nm. The latter are connected by low energy bonds forming huger agglomerates. The carbon black presents a typical microstructure corresponding to interconnected spherical ball of ~100 nm (Figure 2a) having a quite smooth surface (Figure 2b). SAED pattern is composed of two diffused continuous rings. The first ring attests of the periodicity of the carbon planes along c axis whereas the second reveals a beginning of organization within (00l). This carbon planes are rolled up around the center of the particle showing a 2-dimensional organization characteristic of turbostratic carbon.

3.2 The progressive transformation from the reactants towards the final oxycarbide product.

The figure 3a presents the X-ray diffraction patterns obtained on the synthesized powders corresponding to the different values of ξ as reported in table 1. All X-ray patterns have been normalized in intensity based on the (113) peak of the corundum standard. Starting from $\xi=0$ and moving to $\xi=0.7$, it is shown that the intensity of diffraction peaks of hafnia decreases when the ξ value rises while on the opposite, the intensity of the oxycarbide diffraction peaks progressively increases. This observation attests that the progressive consumption of the hafnium dioxide during the reaction is concomitant to the formation of the oxycarbide phase. The oxycarbide

phase that appears from $\xi=0.12$ and the final powder ($\xi=1$) is a single phase compound of oxycarbide. All patterns can be indexed with the JCPDS data file of the hafnium carbide with Fm-3m space group (JCPDS file no 00-039-1491) but it ought to be noted that the diffraction peaks of the oxycarbide phase are slightly shifted towards the low angles of 2θ as the ξ value increases. This information is more conveniently evidenced with the high 2θ angle 511 diffraction peaks (see framed area in Figure 3a and its corresponding enlargement in Figure 3b) for which the phenomenon is emphasized. As for the $\text{ZrO}_2\text{-C}$ system, this peak shift corresponds to a progressive modification of the lattice parameter, the value of the cell parameter rising with the advancement. In this case also, such a phenomenon is linked to the progressive substitution of the oxygen by carbon atoms in the hafnium carbide crystal lattice, the radius of oxygen ($R_{\text{O}} = 0.67 \text{ \AA}$) being inferior to that of carbon ($R_{\text{C}} = 0.74 \text{ \AA}$). However, it is worth to be noted that compared to the $\text{ZrO}_2\text{-C}$ system, the peak shift is limited indicating that the lattice parameter evolution is weak. The figure 3c displays the evolution of the oxycarbide phase lattice parameter a obtained by LeBail refinements. It is to be noted that the values of the cell parameters, obtained at $\xi=1$ ($a_{\text{HfC}_x\text{O}_y} = 4.6378 \text{ \AA} \pm 0.0005$), correspond to that of a nearly stoichiometric carbide ($a_{\text{HfC}} = 4.638 \text{ \AA} \pm 0.005$) [28].

Concerning the hafnia, it is also interesting to compare the XRD patterns acquired on the starting reactant ($\xi=0$) with the one acquired at $\xi=0.12$, *i.e.* solely after a heating at 1650°C without dwell (Table 1). Owing to the low advancement at $\xi=0.12$, the amount of hafnia is not really modified but the shape of the diffraction line profile shows a drastic change (Figure 3d). Whereas the full-width half-maximum (FWHM) of the diffraction peaks is very large at $\xi=0$ ($\text{FWHM} = 0.2235^\circ$), it harshly decreases at $\xi=0.12$ ($\text{FWHM} = 0.0432^\circ$), the line profile being somewhat not so

different than the resolution function of the apparatus. This suggests that the crystal size of hafnia suddenly rises from ~ 17 nm to a few hundred of nanometers at least since the beginning of the dwell. This assumption is confirmed by the TEM study of the evolution of the hafnia behavior with an increasing ξ value (Figure 4). At $\xi=0.12$ the hafnia is characterized by 400 to 500 nm crystallites explaining the evolution of the diffraction peaks profiles. This grain size is very similar to that of the aggregates previously evidenced in the hafnia starting powder. Figure 4 also shows that the crystal size of hafnia progressively decreases with an increasing ξ value, and the crystals progressively acquiring a faceted shape (automorphous character). The crystalline facets were indexed with electron diffraction experiments (Figure 5). Starting from the 4 fold cubic axis, the corresponding images show that (100) and (010) faces are identified being edge on while the two others faces are oblique as wedge fringes are observed parallel to the $\langle 110 \rangle$ type directions. A rotation of the crystal around the b^* axis reveals the appearance of ledges at the periphery of the crystal (see circled area in figure 5b) that are finally viewed edge on in figure 5c. These ledges are formed by the same planes than the crystalline faces limiting the studied crystal, *i.e.* (1 -1 1) and (1 1 1). The same ledges are also observed at the nanometric scale in high resolution images (Figure 5d). As will be discussed further on, these ledges are structural features which can be considered as being at the origin of the destabilization process of the hafnia crystals. The figure 3a shows that the hafnia has almost disappeared at $\xi=0.70$ and should be absent at $\xi=0.8$ as it was the case for the zirconia in the $\text{ZrO}_2\text{-C}$ system. From a thermodynamic view point, is then concluded that hafnia amount is the rate limiting factor for the carbothermal reaction. Finally, it is noticeable that, in contrast with the $\text{ZrO}_2\text{-C}$ system [24], the

automorphous oxycarbide crystals are dislocation free whatever the advancement of the reaction.

The carbon balls also emphasize a change in morphology with the ξ value. Starting from $\xi=0$ which shows rounded carbon balls of 300nm (Figure 4e), the diameter of the sphere decreases (Figure 4f) and the periphery of the particles is no longer smooth but shows the disruption of the external graphitic layers attesting of the destabilization process of the carbon black.

It is finally to be noted that whatever the advancement, no reactional products were ever seen at the contact between carbon and hafnia (Figure 6). The contact between reactants remains no-reactive despite the evidence of destabilization of the hafnia crystallite attested by the presence of numerous ledges on its surface (see small black arrows in Figure 6). The HfC_xO_y oxycarbide is not present between the two reactants but it nucleates within the carbon black regions (Figure 6 see dashed-line arrows). Each nucleus of oxycarbide consists in “core-shell” type particles (Figure 7a-b) where the core is composed of a single crystal of oxycarbide embedded in an amorphous gangue (Figure 7c). Chemical analyses were performed as well as a mapping of the same region in STEM mode (Figure 7d). It is clearly shown that the oxygen is present in the core shell structures. The estimation of the oxycarbide composition based on its cell parameter being rich in carbon, the oxygen amount is certainly very high in the external amorphous layer as it was already the case around Zr-oxycarbides nucleus [24].

The oxycarbide crystallites grow as the advancement of the reaction increases (Figure 8), the external embedding layer being yet present and persisting until $\xi=0.70$. In some regions of the sample, this external rim surrounding the oxycarbide particle has crystallized as shown by the typical moiré effects observed on high

magnification images (Figure 9). This phenomenon was also observed during the carbothermal reduction of ZrO_2 by carbon black [24] but at higher rates of advancement of the reaction (above $\xi=0.80$). Such an external rim disappears at $\xi=1$ (Figure 10) and remnants of it are observed as isolated islands grafted onto the oxycarbide surface (Figure 10c). At the end of the reaction, all the hafnia particles have disappeared (see also Figure 3a). However, some residual carbon is present (Figure 10a) meaning that the final carbide is sub-stoichiometric in carbon. All oxycarbide crystals display the same faceted morphology (Figure 10c) even if those involved in agglomerates (Figure 10b) display more rounded shape, probably due to a coalescence phenomenon or pre-sintering features. The grain size distribution appears uniform. It does not exceed 400 nm and the average size is around 300 nm.

4. Discussion

TEM study of the final product highlights the presence of residual free carbon so that the hafnium oxycarbide is sub-stoichiometric in carbon like the other carbide or oxycarbide compounds issued from the group IV transitional metal.

The observations carried out by TEM on samples selected at different rate of advancement of the reaction show that the contact between hafnia and carbon black is a non-reactive interface. In addition, the nucleation of oxycarbides is strictly localized in the carbon black aggregates. This suggests that this carbothermal reaction is not a solid-solid reaction in which the product is generally developed between reactants. The reactional species need to be forwarded by a gaseous vector towards the oxycarbide formation area. The purely reconstructive character of the carbothermal reduction of hafnia does not allow producing particles which size is lower than 100 nm. The average size of the final product around 300 nm is

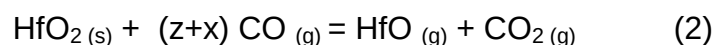
comparable with that obtained by other authors even using other techniques of synthesis [12-13, 22]. Even at low values of the reaction rate ($\xi=0.12$), the grain size distribution of the oxycarbide is important so that the carbothermal route seems inappropriate to synthesize nanometer scale oxycarbides.

The nanometer sized crystallites of hafnia have not allowed getting smaller sized oxycarbides. In fact, the detailed study of the evolution of the hafnia crystallites reveals an abrupt coarsening of the powder during the heating-up of the furnace. It is thus concluded that even if the hafnia dioxide is not the thermodynamically stable form during the synthesis conditions (reductive atmosphere); a grain growth phenomenon arises through coalescence of elementary particles within aggregates in order to reduce the surface energy of the dioxide powder. The coalescence then arises at lower temperature than the carbothermal reaction, meaning that its Gibbs energy is much lower than that required for the carbothermal reaction. The same behavior was already evidenced in the case of the carbothermal reduction of rutile [25]. This result seems to demonstrate that in carbothermal reactions, the original size of the dioxide crystals is not a factor in controlling the expected size of the oxycarbides.

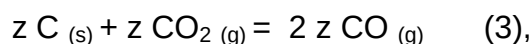
At $\xi=0.12$, the hafnia crystallites show rounded shapes while at $\xi=0.42$, they have acquired faceted automorphous habits decorated with ledges. These particular microstructures are similar to those observed in zirconia treated using a carbothermal reduction [24]. Their occurrence could then be interpreted the same manner, the presence of such structural ledges being associated to the destabilization process of the dioxide compound at the contact of the $\text{CO}_{(g)}$ rich atmosphere [25]. Indeed, the particularity of the destabilization mechanism involved in zirconia is related to its structure and the same process should operate in hafnia, the latter being an isotype

form of zirconia. Summarily, in these compounds the {111} and {100} reticular planes corresponding to the ledges are associated to the more dense planes of the structure. However, it ought to be noted that these planes are very specific as they correspond to an alternation of anionic and cationic layers in a direction normal to these planes. Then, if a {111} or {100} anionic layer is in contact with the surrounding CO_(g) rich atmosphere, the hafnia surface will be reduced, releasing some carbon dioxide. However, the underlying cationic layer is now in direct contact with the reducing atmosphere and could constitute a passivation layer which stops the reaction. The only way to continue the destabilization phenomenon is to break chemical bonds directly at the level of the crystalline ledges. This process which permits the release of hafnia component (hafnium and oxygen) under the form of gaseous specie is accompanied by the migration of the ledges on the surface of the particle (see arrows in figure 5d). From the SSUB5 database [29] and using the Thermo-Calc software, the equilibrium constants of potential reactions between Hf_(s), Hf_(g), HfO_(g), HfO_{2(g)}, HfO_(s) and HfC_(s) was determined and permit to draw the volatility diagram of the Hf-C-O system. The Figure 11 shows at 1650°C the logarithm of the HfO_x pressure as a function of the logarithm of the carbon monoxide pressure. We can easily assume that around hafnia particles, this carbon monoxide pressure is higher than 10 Pascal. This value, indeed corresponds to the boundary of the stability domains of Hf_(g) and HfO_(g). So, the most thermodynamically stable form in our conditions of temperature seems to be the gaseous species HfO.

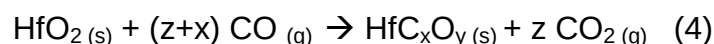
The solid-gas reaction accounting for the destabilization of hafnia can then be written as follows:



On the carbon black reactional site, a disruption of the graphitic layers was observed on the surface of carbon balls. Carbon seems to react with the surrounding atmosphere of carbon dioxide to produce an emission of carbon monoxide according to the equation 1:



the carbon monoxide thus liberated being simultaneously used to destabilize the hafnia through reaction (2). The HfO liberated is achieved through gas medium to the nucleation site of the oxycarbide and the co-condensation of $\text{HfO}_{(g)}$ and $\text{CO}_{(g)}$ leads to the formation of an hafnium oxycarbide phase which nucleates heterogeneously within the amorphous carbon (Figures 6 and 7). The equation (4) describes not only the destabilization phenomenon of HfO_2 but also the nucleation of the oxycarbide phase and corresponds to the global equation of the carbothermal reaction.



At the vicinity of the nucleation site, the co-condensation of $\text{HfO}_{(g)}$ and $\text{CO}_{(g)}$ gives locally rise to high amounts of oxygen which can explain the formation of the amorphous gangue rich in oxygen surrounding the oxycarbide crystals in the early stage of the reaction. When the hafnia dioxide vanishes near $\xi=0.7$ the carbon excess within the sample continues to pump the oxygen from this amorphous layer by the Boudouard equilibrium and when its composition became that of the oxycarbide the external layer crystallizes (Figure 9). This result is then very similar to that observed in the $\text{ZrO}_2\text{-C}$ system [24].

The Rietveld refinements performed to determine accurately the cell parameters were carried out on the global XRD diagrams including the refinement of atomic positions. The results indicated that whatever the advancement rate of the reaction, the oxycarbide shows a face-centered cubic structure with $\text{Fm}\bar{3}m$ space

group and do not confirm the occurrence of a monoclinic intermediate phase [22]. The low shift of the (511) hafnium carbide peak and the low increase of its lattice parameter traduce a limited modification of the composition during the reaction. The lattice parameter increases only slightly of 0.05% between $\xi=0.12$ and $\xi=1$ with the advancement value following a linear function. This result contrast singularly with that obtained on the $\text{ZrO}_2\text{-C}$ system [24]. In this system, if a restricted increase of cell parameter of 0.06% was observed between $\xi=0.2$ and $\xi=0.8$ (the composition was then assumed as constant), a drastic increasing of the cell parameter of 0.2% was observed between $\xi=0.8$ and $\xi=1$. This two-step formation of the oxycarbide phase was also accompanied by a singular evolution of the crystalline habit of the oxycarbides from automorphous dislocation-free crystals to xenomorphous dislocation-bearing crystals. In the case of $\text{HfO}_2\text{-C}$, the oxycarbide is formed through a one-step process and its morphology does not evolve as ξ increases. The crystalline habit corresponds to that of the primary automorphous and dislocation free oxycarbide of the $\text{ZrO}_2\text{-C}$ system. As the hafnium oxycarbide is nearly stoichiometric in carbon at the earliest stage of the reaction there is no need of dislocations. Indeed, their presence in the $\text{ZrO}_2\text{-C}$ system has been justified by the fact that the enrichment in carbon of the ZrC_xO_y oxycarbides above $\xi=0.8$ was assisted by the dislocation motion [24].

This result suggests that the solid solution of oxygen within the hafnium oxycarbide is very limited compared to that in the zirconium oxycarbide. Complementary investigations are now in progress to determine accurately the extent of this solid solution in the HfC_xO_y compounds based on thermodynamic calculations of phase diagrams performed under the CALPHAD method and comprehensive

experimental studies referring to the measurement of the solid solution obtained in both $\text{ZrO}_2\text{-C}$ and $\text{HfO}_2\text{-C}$ systems.

5 – Conclusions

This microstructural approach undertaken on the Hf-C system allows us to compare the results obtained with the mechanisms involved during the carbothermal reduction of zirconia, isotype compound of hafnia.

The numerous similar points between the two systems are as follow:

- The interface between the dioxide and carbon black is non-reactive and the reaction proceeds through solid-gas reactions.
- The oxycarbide phase nucleates in the carbon black area forming some core-shell microstructures exhibiting a crystal core embedded within an amorphous gangue rich in oxygen which crystalizes near of $\xi=0.7$.
- Then this gangue disappears between $\xi=0.7$ and $\xi=1$ when the hafnia is consumed and that thanks to a progressive reduction of the oxycarbide which is continued owing to the carbon excess.

The main difference between the two systems concerns the growth step of the oxycarbide phase. While in $\text{ZrO}_2\text{-C}$ system the oxycarbides are obtained through a process involving two steps, in the $\text{HfO}_2\text{-C}$ system, only one generation of oxycarbide is formed, its composition being rich in carbon at the early stage of the reaction. This result highly suggests that the oxygen solubility is very low in the HfC_xO_y compared to ZrC_xO_y .

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Tables

Advancement ξ	Temperature ($^{\circ}\text{C}$)	Dwelling Time
0.12	1650	No dwell
0.42	1650	30 min
0.70	1650	1 h
1	1650	2 h
1	1650	8 h
1	1800	1 h

Table 1

Table 1: The different heat treatments and their corresponding advancements ξ

Figure captions:

- Figure 1: Characterization of the hafnia starting powder.
 (a) X-Ray diffraction pattern of the initial hafnia powder,
 (b) TEM general view of the hafnia powder and its SAED pattern,
 (c) TEM view of aggregates (1) and agglomerates (2) in starting hafnia powder.
- Figure 2: Observation by TEM of the carbon black starting powder.
 (a) General overview,
 (b) Enlargement on carbon balls and their SAED pattern
- Figure 3: X-ray diffraction results obtained either on reactive or products at different ξ values.
 (a) X-Ray diffraction patterns of starting hafnia and of the different powders obtained at different advancements of the reaction mixing with an internal standard (Al_2O_3).
 (b) Enlargement of the framed area in (a) corresponding to the (511) diffraction peak of the hafnium oxycarbide.
 (c) Evolution of hafnium oxycarbide lattice parameter with respect to the rate of the reaction ξ .
 (b) Enlargement of the framed area in (a) corresponding to the (-111) diffraction peak of the hafnium dioxide.
- Figure 4: TEM observations of the morphological evolution of starting reactants during the reaction:
 hafnia (a) $\xi = 0$, (b) $\xi = 0.12$, (c) $\xi = 0.42$, (d) $\xi = 0.7$
 carbon black (e) $\xi = 0$, (f) $\xi = 0.42$
- Figure 5: Tilting experiments to determine the indexation of the crystalline faces and ledges at the surface grain of the hafnia crystals ($\xi = 0.42$)
 a: Image and its associated SAED pattern under $[00\bar{1}]$ zone axis.

- b: Image and its associated SAED pattern under $[10\bar{1}]$ zone axis.
c: Image and its associated SAED pattern under $[10\bar{2}]$ zone axis.
d: High resolution image obtained with the $[10\bar{1}]$ zone axis and showing the existence of ledges at the nanometric scale.

Figure 6: TEM observations performed at $\xi = 0.42$ showing the contact between a hafnia crystallite and the neighboring carbon black balls. The hafnia crystallite show numerous ledges on its surface (see black arrows). The nucleation sites of the oxycarbides are situated within the carbon black areas of the sample (see dashed-line arrows).

Figure 7: TEM observations showing the nucleation site of the oxycarbides ($\xi = 0.42$).
(a) TEM overview of a nucleation site.
(b) Enlargement on nuclei located within carbon black.
(c) High resolution TEM image of the nuclei covering layer and its associated SAED pattern.
(d) EDX mapping of the nucleation site in STEM mode.

Figure 8: TEM observation of a hafnium oxycarbide particle at $\xi = 0.7$
(a) General overview.
(b) Enlargement of the rim of the crystal showing the presence of an amorphous layer in the circled region of (a).

Figure 9: TEM observation of an oxycarbide particle showing the crystallization of its external surrounding layer as HfC_xO_y nanocrystallites ($\xi = 0.7$)
(a) General overview.
(b) Enlargement of the rim corresponding to the rectangular area reported in a) showing the typical moiré effect.

Figure 10: TEM observation of a hafnium oxycarbide particle at $\xi = 1$
(a) TEM overview of the final product containing hafnium oxycarbide and residual free carbon.
(b) Observation of agglomerates in the final powder.

(c) Enlargement of a hafnium oxycarbide particle and its corresponding SAED pattern (d).

Figure 11: Volatility diagram of the Hf-C-O system at 1650 °C as a function of the carbon monoxide pressure.

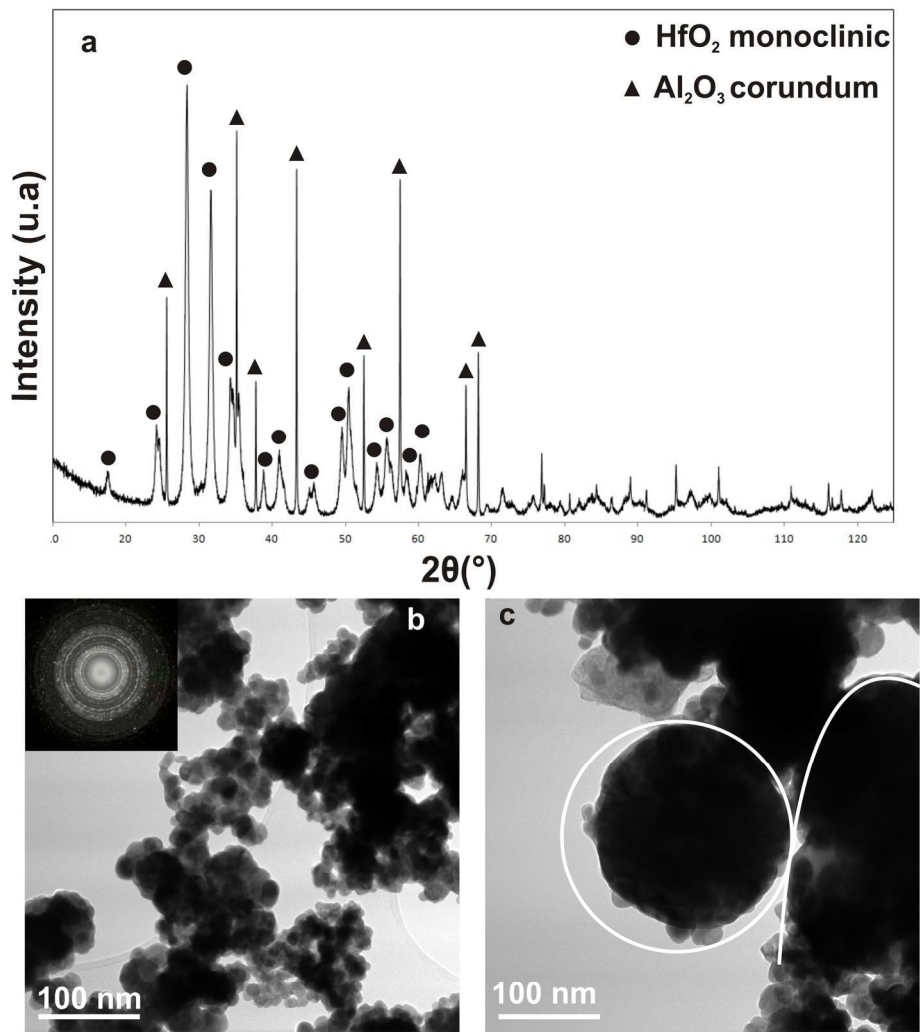


Figure 1

165x218mm (300 x 300 DPI)

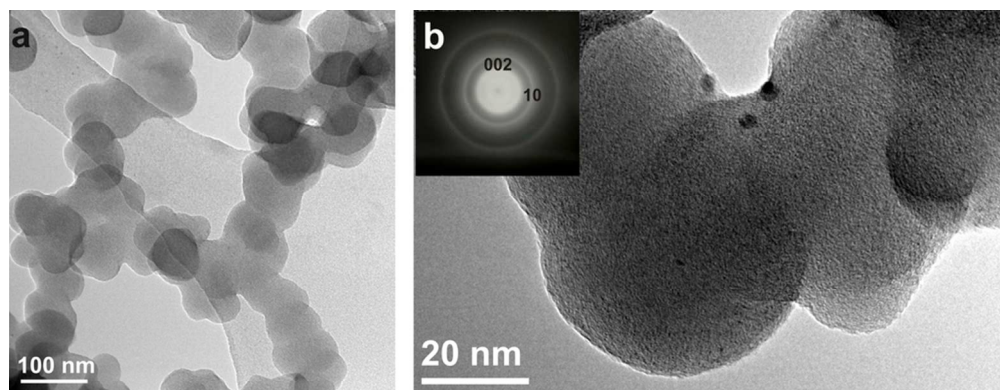


Figure 2

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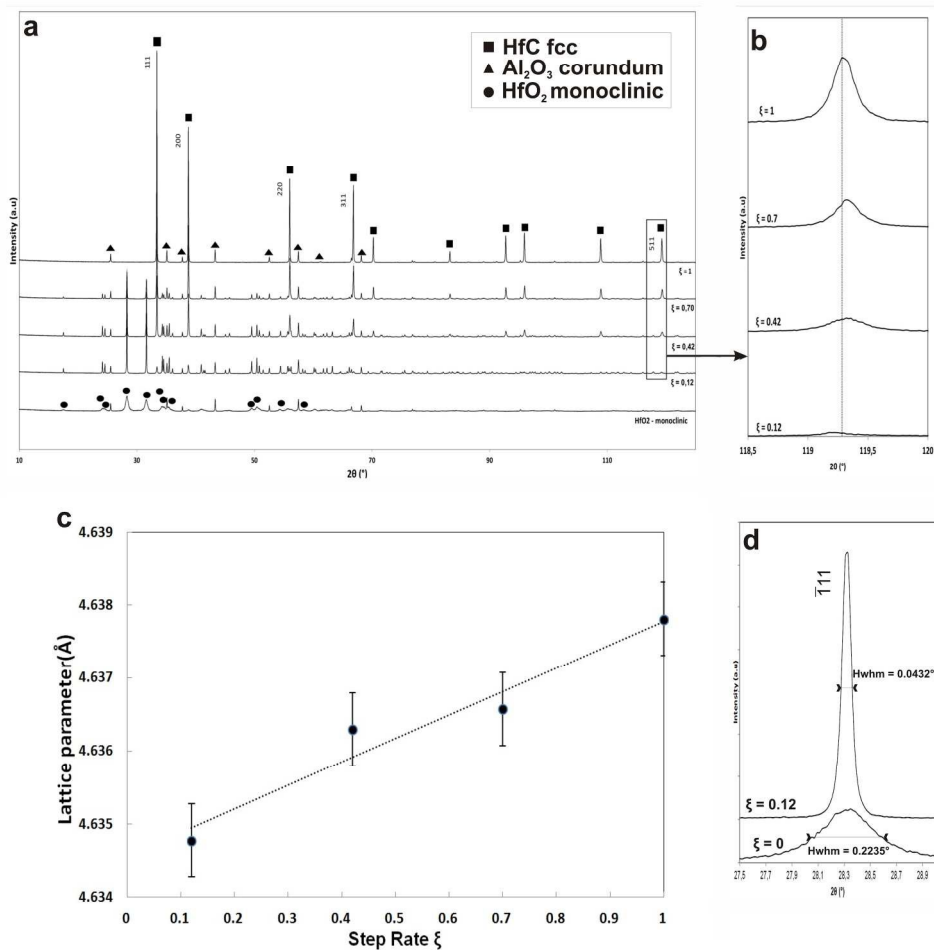


Figure 3

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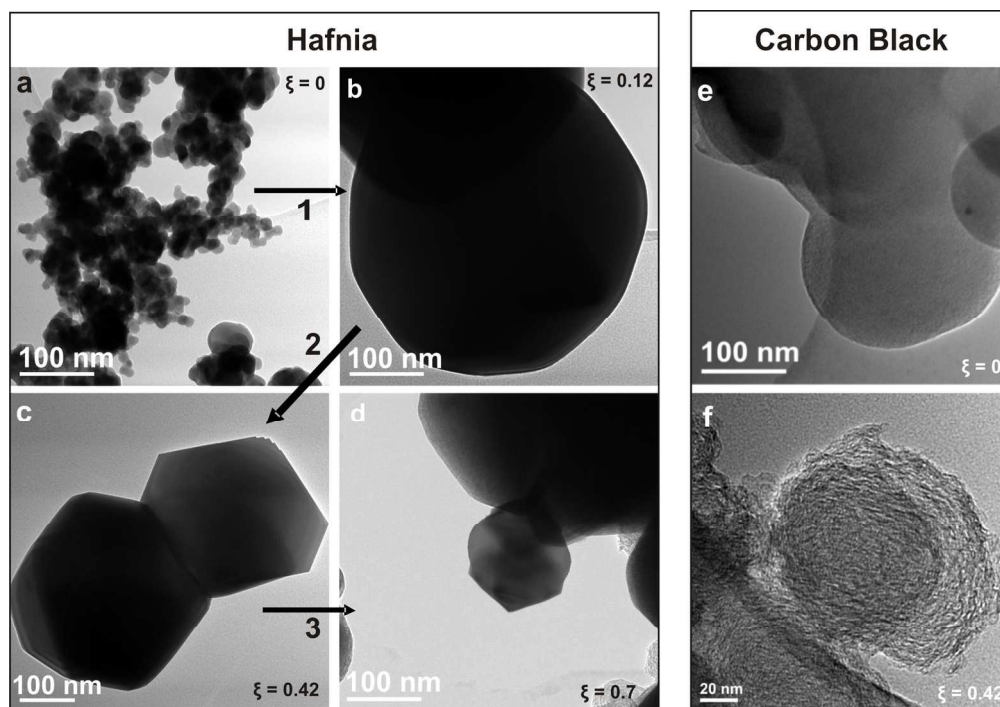


Figure 4

154x126mm (300 x 300 DPI)

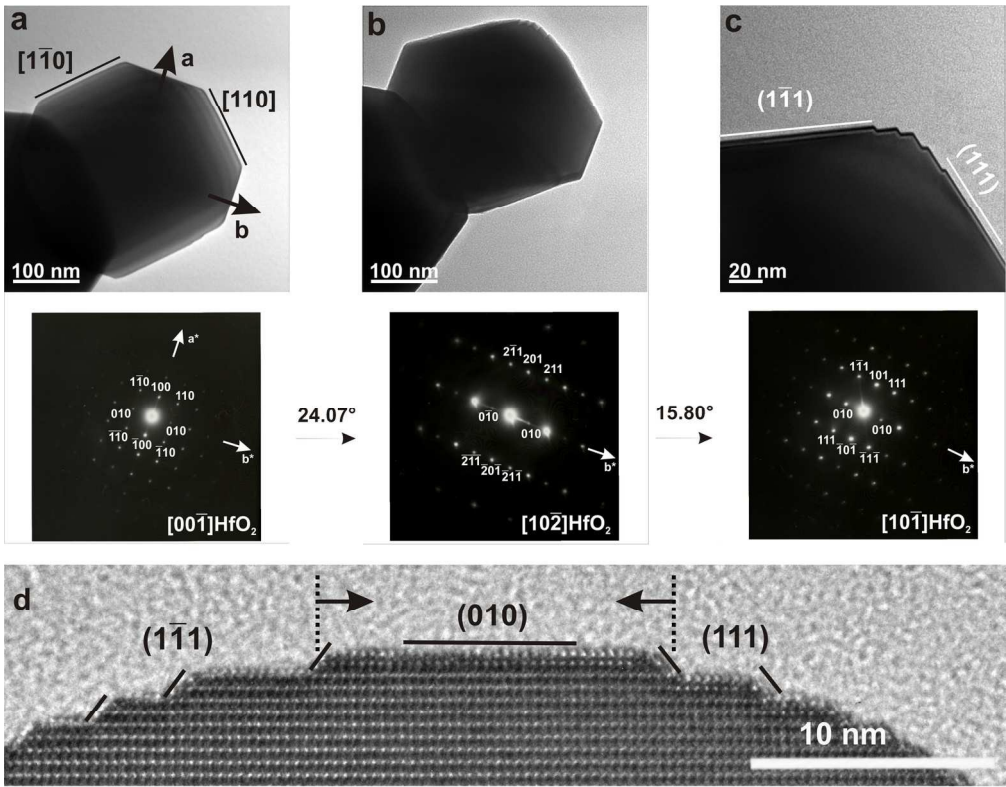


Figure 5

158x143mm (300 x 300 DPI)

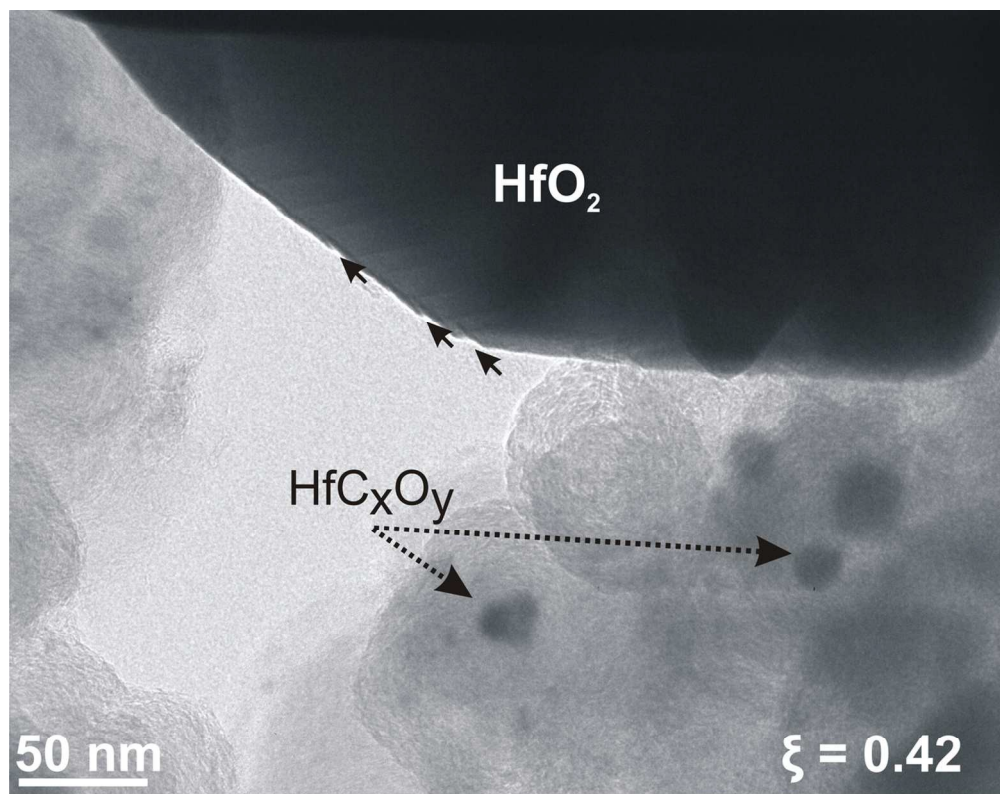


Figure 6

124x115mm (300 x 300 DPI)

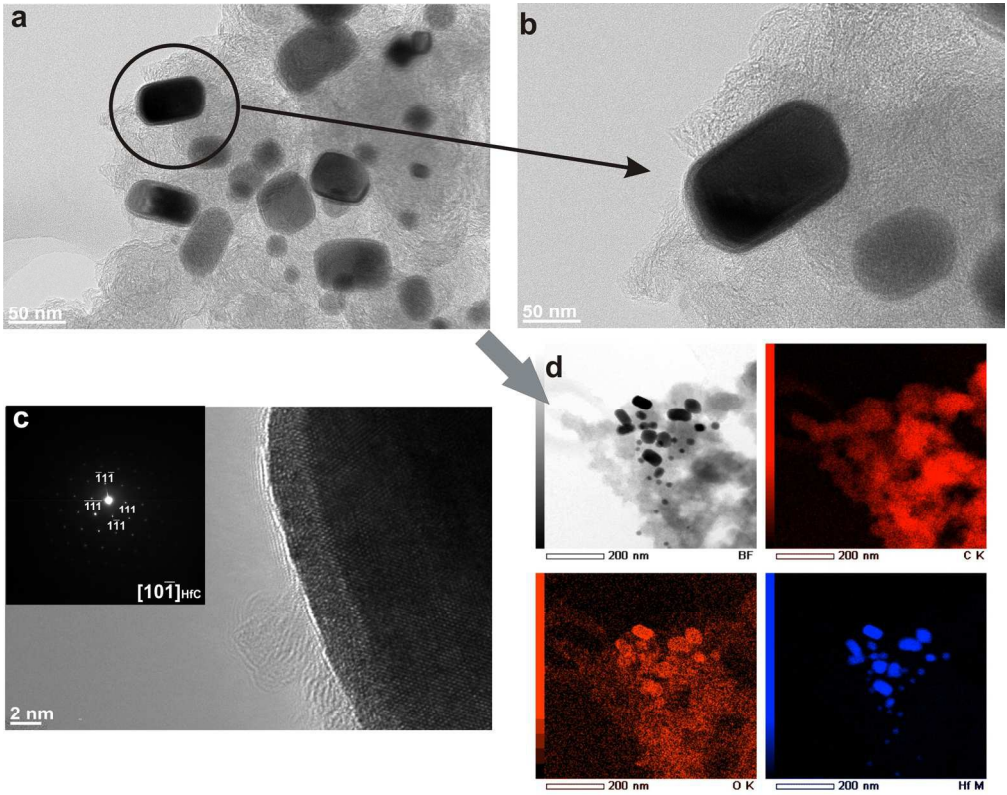


Figure 7

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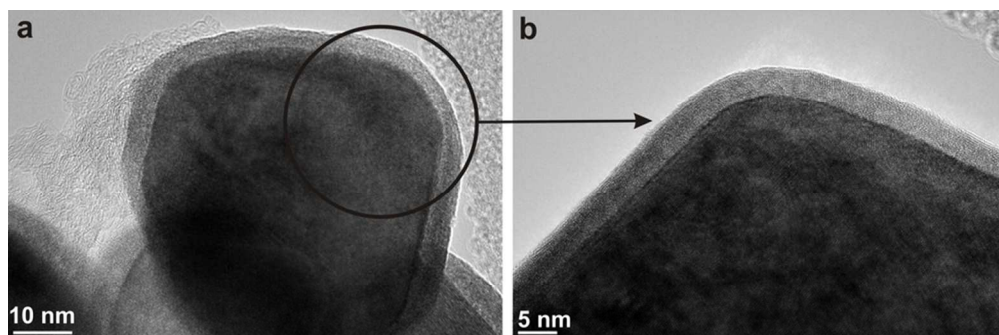


Figure 8

83x38mm (300 x 300 DPI)

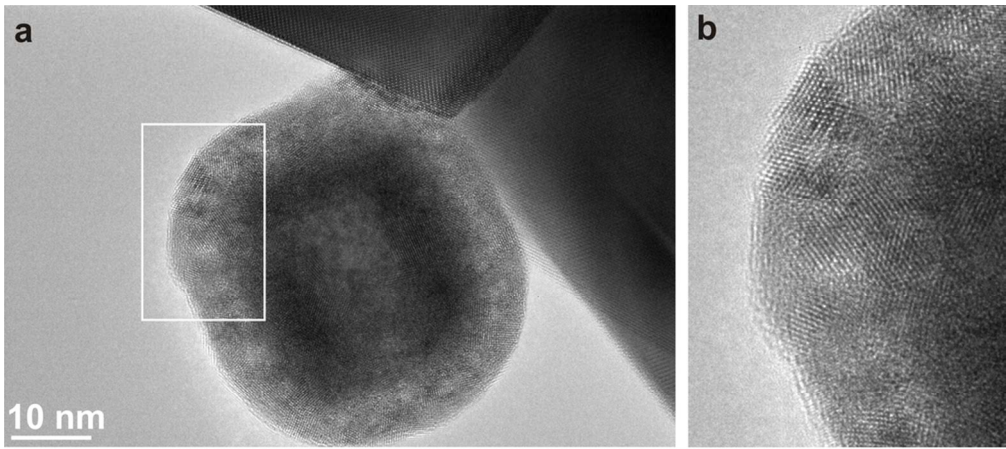


Figure 9

95x55mm (300 x 300 DPI)

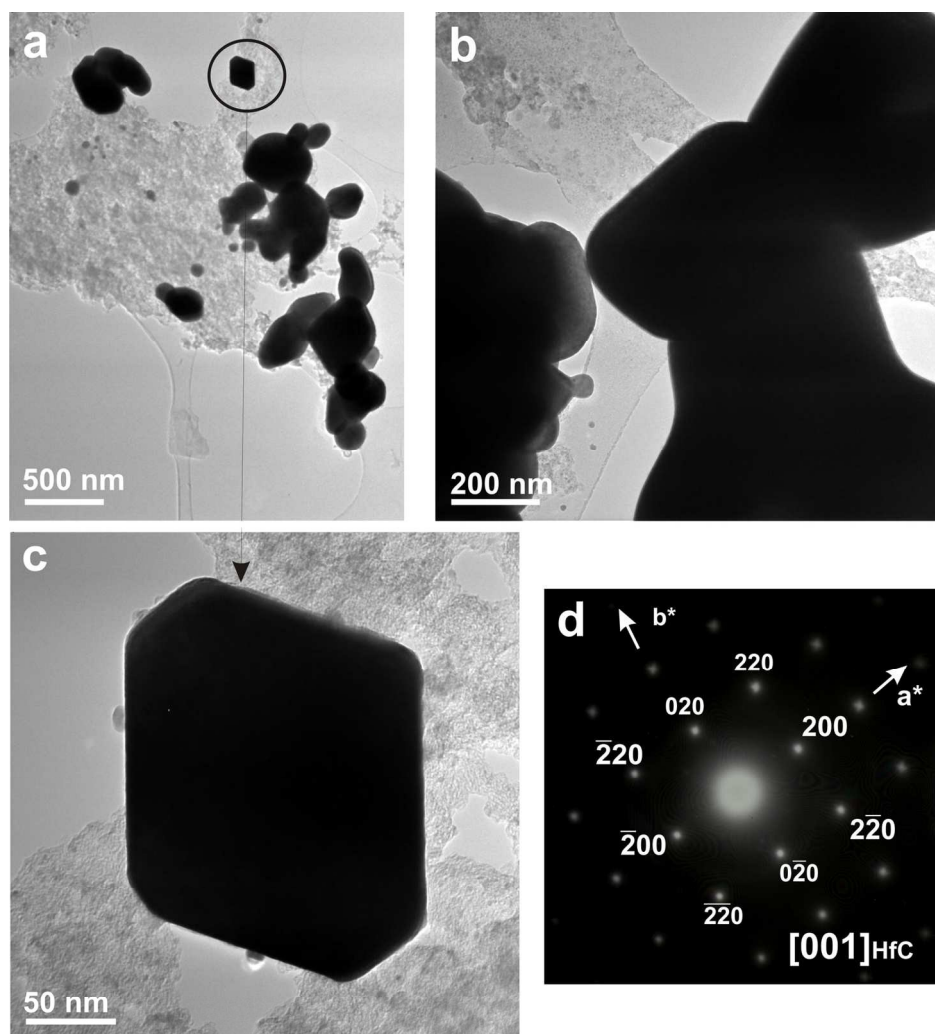


Figure 10

141x181mm (300 x 300 DPI)

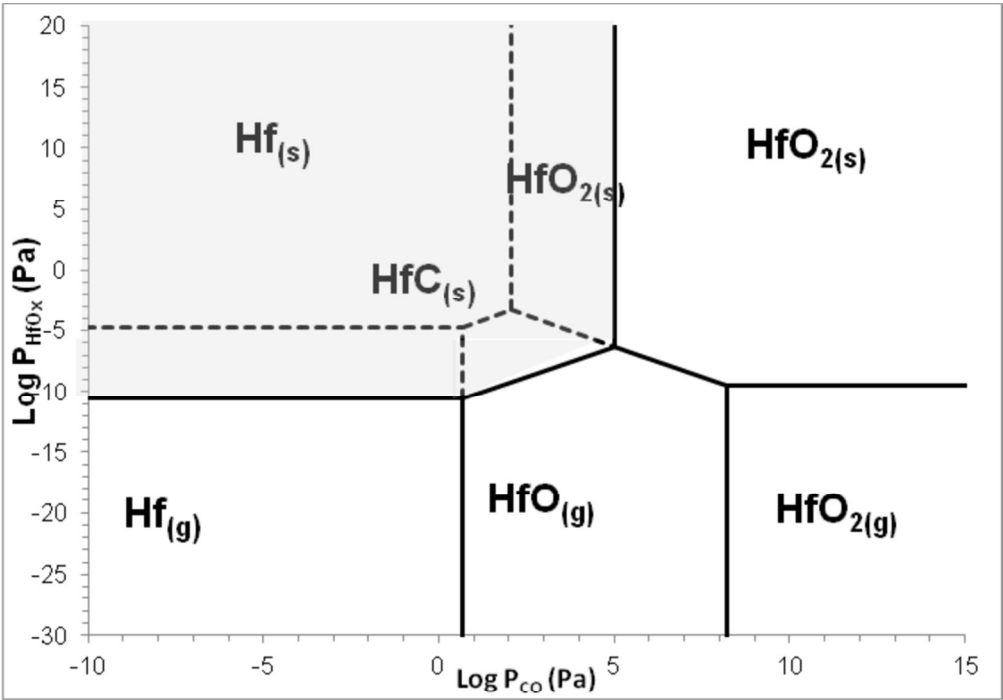


Figure 11

94x83mm (300 x 300 DPI)