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Feature article

Phase transformations and microstructural features in hafnium nitrides

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ABSTRACT

Two sets hafnium nitride diffusion couples processed by hot-isostatic pressing at 1200 °C and 1900 °C were formed by reacting Hf with HfN. The 1900 °C couple consisted of Hf grains next to ϵ -Hf₃N₂ grains with fine Hf laths. These were followed by refined ζ -Hf₄N₃ grains abutted to the equiaxed HfN grains that had a precipitated crisscross pattern of ζ -Hf₄N₃ laths on the close-packed planes of HfN; this microstructure agreed with a model's prediction that these interfaces are the most thermodynamically favorable nucleation sites. The 1200 °C couple revealed similar regions except for a lack of this crisscross ζ -Hf₄N₃ lath morphology in HfN. The lower temperature is suspected to kinetic limit the condensation of nitrogen vacancies necessary to facilitate lath precipitation. A range of lattice parameters were found to occur for the ϵ -Hf₃N₂ and ζ -Hf₄N₃ phases within the couple indicating that these nitrides are not line compounds but accommodate some amount of stoichiometry variation.

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1. Introduction

Ultra high temperature ceramics (UHTC) constitute a class of materials characterized by high melting points, chemical inertness, high hardness, and moderate oxidation resistance [1–3]. These ceramics typically comprise either group IVB or VB metals bonded with boron, carbon or nitrogen [2]. When in an equal atomic ratio, a MX compound will nominally form, where M is the metal species and X the interstitial light element (boron, carbon, or nitrogen). Dependent on the light species type, the group IVB and VB metals can precipitate metal-rich M₆X₅, M₄X₃, M₃X₂, and/or M₂X compounds. The precipitation of these phases have a dramatic influence on the microstructure's grains' morphology [2–6] and properties, including mechanical [7,8], electrical [9] and oxidation [10,11]. Intrinsic to microstructure manipulation, i.e. properties, is regulating the precipitation and growth of these secondary phases. For example, in tantalum carbides, the precipitation of the Ta₄C₃ phase from TaC results in a crisscross pattern of laths within equiaxed grains whereas Ta₄C₃'s precipitation from Ta₂C results in the laths parallel to each other and along the major axis of the acicular grains [5]. To engineer microstructures,

quantifying the microstructure types and formations that result from secondary phase precipitation is essential for manipulating structure-property relationships. In the current work, the microstructure formations between various hafnium nitride phases are explored to determine what morphologies are present in multiphase fields and how microstructures evolve when mixed phase powders are in contact with each other.

For the Hf-N system, the incorporation of nitrogen strengthens the intrinsic bonding in hafnium evident by the increase in melting temperature of the hexagonal close packed (HCP) α -Hf phase (*P6₃/mmc*) from 1743 °C to 2910 °C [12–14], Fig. 1(a). From approximately 43 at.% N to slightly above 50 at.% N, the mononitride δ -HfN is stable with the B1 or face-centered cubic (FCC) based rock-salt crystal structure (*Fm $\bar{3}m$*) is shown in the phase diagram. In a very recent computational report on the phase stability in the Hf-N system, this HfN phase was predicted to actually be *P6₃/mmc* whereupon above 670 K, the rocksalt B1 crystal structure became favorable [15]. To the authors' knowledge, the *P6₃/mmc* HfN has not been experimentally observed.

It is interesting to note that the δ -HfN phase is stabilized for slightly nitrogen-rich compositions. Though Fig. 1(a) indicates this to be the same B1 phase, this nitrogen-rich crystal structure has been found to be dependent on the temperature and pressure by which it is processed [16]. Dependent on process, which includes chemical vapor deposition [17] and atomic layer deposition [18,19]

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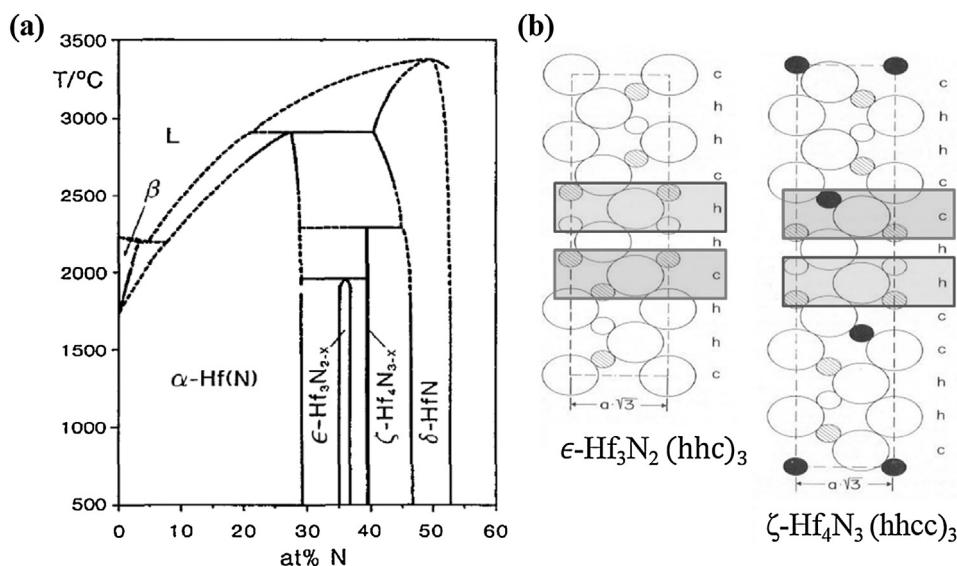


Fig. 1. Phase diagram of (a) Hf-N system [27] (b) Crystallographic $[11\bar{2}0]$ view of ζ -Hf₄N₃ and ϵ -Hf₃N₂ demonstrating alternating hexagonal (h) and cubic (c) layers bonded along the interstitial vacancies based on Rudy (1970) [23]. The subscript for the 'h' and 'c' stacking represents the repeat unit for the stacking sequence.

as well as in laser-assisted heated diamond anvil cells [20], the Hf₃N₄ phase has adopted the Th₃P₄-type ($I\bar{4}3d$) [20], the tetragonal $I4/m$, or $Pnma$ structures. First principle computational predictions, at 0K, predict that this Hf₃N₄ phase to be $Pnma$ at ambient pressures [9,21] and the Th₃P₄-type structure above 9GPa [22].

Upon sufficient reduction of nitrogen, the mononitride phase becomes thermodynamically unstable and results in the precipitation of various hafnium-rich nitride phases. These phases will be the subject of this paper. As with the nitrogen-rich phase, the hafnium-rich phases have had some debate about their stability and structure types. It was previously believed by Rudy and Nowotny that only a hexagonal-based Hf₂N structure was present between α -Hf and δ -HfN [12]. However, Rudy revised these earlier findings and established that two rhombohedral phases ($R\bar{3}m$), ζ -Hf₄N₃ and ϵ -Hf₃N₂ (which has also been referred to as the eta-phase in later reports), existed and Hf₂N was not present [23]. This confusion lies in that these phases have very similar stacking sequences to each other [24].

When the M₂X structure is generically represented in a hexagonal close packed (hcp) setting, the different stacking sequences of the metallic atoms result in different spatial arrangements of the octahedral interstices, where the light element X resides, as compared to the MX phase. The octahedral interstices form straight chains running parallel to the *c*-axis with vacancies and interstitial atoms alternating along these chains [23, Fig. 1(b) [25]. In contrast, larger spacing's can exist between interstitial sites in the face centered cubic (fcc) based MX phases [23], where all the light element sites may be occupied. Since both types of interstitial atom packings are possible, *i.e.* hcp versus fcc, in the ϵ -Hf₃N₂ and ζ -Hf₄N₃ structures, this lead to the apparent confusion. In ζ -Hf₄N₃, the nitrogen resides in three hexagonal based interstitial sites and two cubic based interstitial sites along the *c*-axis [23,24]. For the ϵ -Hf₃N₂, the nitrogen resides in three hexagonal and one cubic interstitial site. This can be seen in the comparative drawing shown in Fig. 1(b) [25].

In earlier phase diagrams of Hf-N system, the ζ -Hf₄N₃ phase was considered to only be stable at temperatures in excess of approximately 1225 °C where upon it would decompose into either the ϵ -Hf₃N₂ or δ -HfN phases at lower temperatures [14]. However, these findings were also subsequently updated on the phase diagram by the work Lengauer et al. [26,27]. In their paper, a diffusion couple created from the annealing of hafnium in a nitrogen environment resulted in evidence that both ϵ -Hf₃N₂ and ζ -Hf₄N₃ were

low temperature stable phases that existed between 33–47 at.% N, which is between the α -Hf and δ -HfN phase fields in Fig. 1(a) and noted by Rudy [23]. Furthermore, these phases have also been shown to form as single phase grains [26] with compositional capacity for deviations from stoichiometry [27].

This hafnium-rich nitride phase stability has been further studied in the computational work by Zhang et al.'s [15]. They predicted, at 0K, the $P\bar{3}1c$ Hf₆N, $P6_322$ Hf₃N, $Pnmm$ Hf₂N, $R\bar{3}m$ Hf₃N₂, and $R\bar{3}m$ Hf₄N₃ phases. The Hf₆N, Hf₃N, and Hf₂N phases are a nitride ordering structure where the metal atoms have an hcp arrangement and the nitrogen atoms order in the octahedral interstices. These structures, like $P6_3/mmc$ HfN, have not been experimentally observed. It is likely that entropic effects with increasing temperature contribute to the instability of these phases, which has been noted in similar vacancy ordered transition metal carbides [28–31].

Though both computational [15] and experimental [27] studies have been reported in the Hf-N systems, to date, there has not been a rigorous experimental study that quantifies the microstructural evolution created by the phase transformation pathways. This is surprising considering that the metal-rich nitride phases appear to intrinsically regulate the self-organization of nitrogen to specific interstitial sites and can precipitate out nano-laminate phases [16] which could be strengthening mechanisms in the microstructure. For example, in tantalum carbides a high fraction of the $R\bar{3}m$ ζ -Ta₄C₃ faulted phase forms as nanoscale laths that significantly increase the fracture toughness by constructing a tortuous crack path within the microstructure [32]. Since the group VB transition metal carbides and the transition group IVB metal nitrides share equivalent phases, determining if similar microstructures exist between these two classes of UHTCs would be informative in engineering potential structure-property connections.

In the present study, diffusion couples have been fabricated between α -Hf and δ -HfN under hot-isostatic pressing (HIP) to determine these phase transformation pathways and their resulting microstructures. HIP is commonly used as a fabrication method for UHTCs and would provide a direct comparative study in processing-structure relationships in how various multiphase microstructures form from the depletion of nitrogen from one phase and its migration (and reaction) with another phase. The prior experimental couple by Lengauer et al. [27] involved annealed hafnium sheet in a nitrogen atmosphere. Thus, the HIP'ed couple would yield new insights into the processing-structure rela-

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