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Synthesis and properties of oxygen-bearing c-Zr_3N_4 and c-Hf_3N_4

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ABSTRACT

This paper presents our recent results on synthesis and properties of high-pressure cubic zirconium(IV)- and hafnium(IV) nitrides having Th_3P_4-type structure, c-M_3N_4 (M = Zr or Hf). c-M_3N_4 were first synthesized in microscopic amounts in a laser-heated diamond anvil cell (LH-DAC) at pressures above 15 GPa and temperatures above 2500 K. Further, macroscopic amounts of c-Hf_3N_4 and of a new oxygen-bearing zirconium nitride, c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$, were synthesized at 12 GPa and about 1900 K using a multi-anvil apparatus. The lattice parameter of c-Hf_3N_4 was determined to be $a_0 = 670.2(1)$ pm. The a_0 of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ of 675.49(1) pm was found to be slightly larger than that of c-Zr_3N_4 (674.0(6) pm). The bulk moduli, B_0, of 219 GPa for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ and of 227 GPa for c-Hf_3N_4 were obtained from compression measurements. Combining the compression and indentation data we determined for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ its isotropic shear modulus $G_0 = 96$ GPa. Finally, Vickers microhardness, indentation fracture toughness and thermal expansion of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ were measured.

1. Introduction

The group 4 transition metal mononitrides δ-MN (where M is Ti, Zr or Hf) having cubic NaCl-type structure are well known refractory materials with unique combinations of mechanical, thermal, chemical and electro-magnetic properties. They have found a broad industrial application as hard wear resistant coatings of cutting tools, corrosion and abrasion protection layers on mechanical and optical components, diffusion barriers and superconductors in microelectronics [1,2]. With respect to stoichiometric M_3N_4 compounds of the group 4 elements, only orthorhombic zirconium nitride, o-Zr_3N_4, was known for a long time [3–5].

Here we review our work on synthesis, characterization and investigation of properties of novel cubic Zr_3N_4 and Hf_3N_4. These nitrides were first obtained via chemical reactions of zirconium and hafnium or their mononitrides (δ-MN) with molecular nitrogen at high pressures (>15 GPa) and high temperatures (>2500 K) in a LH-DAC [6]. Examination of the structure and stoichiometry of the products using XRD and EDX revealed that the reaction products were stoichiometric nitrides Zr_3N_4 and Hf_3N_4 with cubic Th_3P_4-type structure (space group $I\bar{4}3d$, No. 220) [6]. It should be pointed out that c-Zr_3N_4 and c-Hf_3N_4 are the first binary nitrides with eightfold coordinated cations [6]. Preliminary compressibility measurements have indicated high bulk moduli, B_0, of about 250 GPa (with $B_0' = 4$) for both compounds thus suggesting their high hardness.

Subsequent theoretical studies of these transition metal nitrides supported the structure assignment and a low compressibility of c-M_3N_4 [7–9]: The B_0 values of 195–265 GPa and 215–283 GPa were predicted for c-Zr_3N_4 and c-Hf_3N_4, respectively. Using these results and an empirical correlation between hardness and elastic moduli [10], Mattesini et al. [8] suggested the Vickers hardness value of about 20 GPa for the both compounds. Further interest in these materials was excited by the finding that thin films of c-Zr_3N_4 are significantly harder than those of δ-ZrN and dramatically outperform δ-TiN (by one order of magnitude) in wear resistance by

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machining of low-carbon steels [11]. Titanium mononitride, in turn, is a well-known hard wear-resistant material which is traditionally used in mono- and multilayer coatings of cutting and milling tools because it considerably increases their service life [12,13]. The films of pure c-Zr_3N_4 were prepared via the technique of physical vapour deposition (PVD) by applying a modified filtered cathodic arc method [11]. The authors were able to control the stoichiometry and the structure of the nitrides and to deposit stoichiometric δ-ZrN or Zr_3N_4 with either orthorhombic or cubic structure. These results demonstrated a great potential of c-M_3N_4 for industrial application as hard wear-resistant coatings.

Very recently we succeeded in synthesis of macroscopic amounts (>1 mm^3) of oxygen-bearing cubic zirconium(IV) nitride, c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ [14], as well as of c-Hf_3N_4 at high pressures and temperatures. The obtained materials were examined using the XRD-, TEM-, EPMA- and SEM-techniques. The results are described below. We also present accurate values for B_0 of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ and c-Hf_3N_4 derived from their equations of state (EOS), $V(P)$, measured on compression at RT [15,16]. Applying nanoindentation technique we obtained the reduced elastic modulus, E_r, and hardness, H, of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$. Combining the results for B_0 and E_r we derived the shear modulus, G_0, for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ [15]. Hardness and fracture toughness of porous oxygen-bearing c-Zr_3N_4 were determined from Vickers indentation testing. Finally, the first results on thermal expansion of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ from high-temperature XRD measurements will be described.

2. Experimental methods

The high-pressure high-temperature synthesis of macroscopic amounts of oxygen-bearing c-Zr_3N_4 and of c-Hf_3N_4 was performed in a multi-anvil apparatus. As a starting material we used nanocrystalline powders of nitrogen-rich zirconium and hafnium nitrides (N:M > 1.33) having distorted NaCl-type structure [17]. The starting materials in platinum capsules were compressed to 12 GPa and heated up to 1900 K, kept at the maximum temperature for about 20 min and quenched. The recovered products were characterized using an electron probe micro-analyzer CAMECA SX-50, a scanning electron microscope Philips XL30 FEG and a TEM Philips CM20 equipped with an EDX-detector. The powder X-ray diffractograms of high-pressure nitrides were collected using a STOE STADI P diffractometer with Mo-$K_{\alpha1}$ radiation.

The EOS of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ and c-Hf_3N_4, synthesized in a multi-anvil apparatus [14] and in a LH-DAC [6], respectively, were measured on compression at RT in a DAC to about 45 GPa. Argon was used as quasi-hydrostatic pressure medium. Pressure values were determined from the EOS of crystalline argon [18]. Specific volumes of the sample material and of argon at high pressures were derived from the EDX powder diffraction patterns measured using a polychromatic synchrotron radiation (beam-line F3 at the HasyLab, DESY, Hamburg, Germany).

Nanoindentation testing was carried out on a polished surface of the porous polycrystalline c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ using Nanoindenter XP equipped with the continuous stiffness measurement (CSM) module [19]. Experiments were performed to two maximum loads of about 23 mN and 14 mN which corresponded to maximal indentation depths of about 260 nm and 210 nm, respectively. In the Vickers hardness measurements the loads between 0.49 N and 9.8 N were applied. Thermal expansion of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ was examined to 873 K using a STOE STADI P X-ray diffractometer equipped with a curved imaging plate position sensitive detector.

3. Results and discussion

The XRD examination of the zirconium nitride product synthesized in a multi-anvil apparatus showed only lines of a cubic phase having Th_3P_4-type structure (Fig. 1). The EPMA revealed presence of a minor amount of oxygen (mass fraction of 0.024). Since in the TEM investigations no amorphous oxidic layers were observed on the grain surfaces, we concluded that oxygen was incorporated in the crystal structure and the composition of the product could be expressed as $Zr_{2.86}(N_{0.88}O_{0.12})_4$. This suggested formation of an oxygen-bearing cubic zirconium(IV) nitride of the general composition $Zr_{3-u}(N_{1-u}O_u)_4$. Here, formation of vacancies at the cation sites required by the condition of electrical neutrality is taken into account. This supposition was verified by a

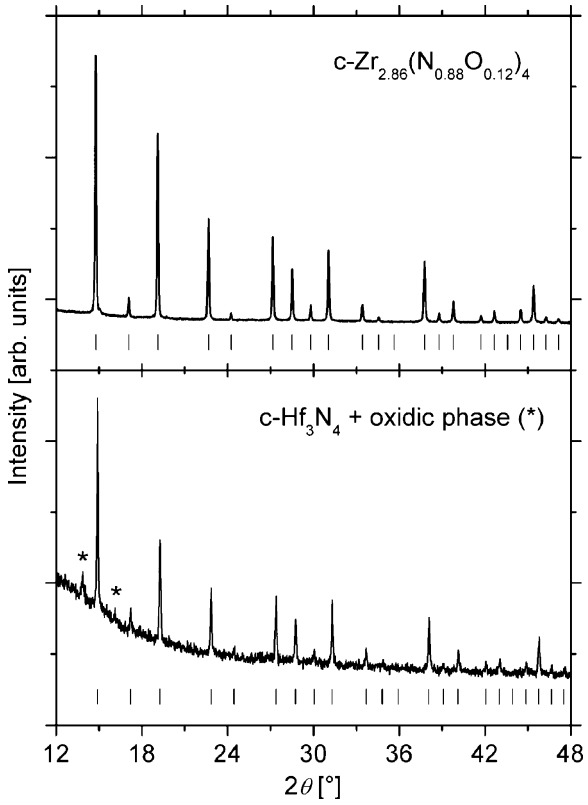

Fig. 1. Powder XRD patterns of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ (top) and c-Hf_3N_4 (bottom) synthesized at 12 GPa and 1900 K in a multi-anvil apparatus. The Bragg positions of the Th_3P_4-type phases are displayed below the patterns. The asterisks denote the XRD reflexes from an oxidic impurity in the hafnium nitride sample.

full-profile Rietveld structure refinement of the XRD data (Fig. 1) [14]. The lattice parameter of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ was found to be $a_0 = 675.49(1)$ pm which is slightly larger than $a_0 = 674.0(6)$ pm reported earlier for c-Zr_3N_4 [6]. This observation contradicts to an expected decrease of a_0 due to both substitution of N^{3-} by O^{2-} anions having smaller ionic radius and formation of cation vacancies. However, recent theoretical calculations have shown that incorporation of oxygen in c-M_3N_4 (M = Zr or Hf) results in a weakening of the cation-anion bonding [20]. This leads to reduction of elastic moduli of oxygen-bearing c-M_3N_4 and, on reaching of a critical oxygen concentration, to expansion of the unit cell [20]. The formation of cation vacancies, however, was not considered in the calculations.

The EPMA detected a minor amount of oxygen (mass fraction of ~0.02) in hafnium nitride sample as well. However, in contrast to oxygen-bearing c-Zr_3N_4, results of XRD-, SEM- and EDX-analyses revealed the presence of a crystalline hafnium oxide or oxynitride, in addition to c-Hf_3N_4. The nature of the contaminating oxidic phase could not be determined unambiguously due to a low intensity of its XRD reflexes (Fig. 1). The lattice parameter of c-Hf_3N_4 of $a_0 = 670.2(1)$ pm was found to be in agreement with that reported earlier ($a_0 = 670.1(6)$ pm) [6]. If a_0 of c-M_3N_4 is influenced by substitution of nitrogen by oxygen [20], it should be recognized that, in contrast to zirconium, cubic hafnium(IV) nitride precludes oxygen incorporation in the structure. Influence of oxygen impurities on the lattice parameter and properties of c-M_3N_4 could be a subject of future experimental and theoretical work.

The $V(P)$ dependences of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ and c-Hf_3N_4 measured at RT in a DAC to about 45 GPa [15,16] are shown in Fig. 2. From the least-square fit of the Birch-Murnaghan EOS [21] to the experimental data we obtained $B_0 = 219(13)$ GPa, $B_0' = 4.4(10)$ and

$B_0 = 227(7)$ GPa, $B_0' = 5.3(6)$ for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ and c-Hf_3N_4, respectively. For B_0' fixed at 4 we obtained $B_0 = 224(5)$ GPa for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ and 241(2) GPa for c-Hf_3N_4. The theoretical predictions for B_0 of c-M_3N_4 [7–9] scatter around our experimental values.

SEM investigations have shown that our samples were highly porous with pore sizes of 0.05–2 μm. The average volume fraction porosity (VFP) was estimated to be about 0.25–0.3 for both zirconium- and hafnium-nitride products. Nanoindentation measurements on a polished surface of the porous c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ gave $E_r = 231$ GPa and $H = 18(2)$ GPa [15]. Using the experimental values for B_0 and E_r and the well-known relations between isotropic E_r, E, B, G, and ν [22] we determined for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ $G_0 = 96$ GPa and $E_0 = 252$ GPa [15]. The obtained values should be considered as the lower limits since they could be altered by porosity. We were also able to perform reliable Vickers microhardness measurements for our porous c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ and obtained $H_V(1) = 12.0(6)$ GPa [14]. This value is similar to $H_V(1)$ of single crystal δ-ZrN (12.2 GPa) [23] but about 2.5 times higher than that for porous polycrystalline δ-ZrN with the VFP of ~0.18 [24]. Based on the known hardness-porosity relations for hard ceramic materials [24,25], we estimated the H_V value of fully dense c-Zr_3N_4 to exceed 30 GPa.

For high indentation loads (≥2.94 N) our SEM investigations revealed presence of radial cracks having their origin at the corners of the Vickers impressions. The crack lengths were used for estimation of the indentation fracture toughness, $K_{Ic\text{-}if}$, of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ according to the equations of Niihara et al. [26] and Shetty et al. [27]. The average value of $K_{Ic\text{-}if}$ was derived to be 3.2(3) MPa $m^{1/2}$ which is slightly lower than $K_{Ic\text{-}if}$ reported for hot-isostatically pressed δ-MN [28–30]. As above for other elasto-mechanical values, the present $K_{Ic\text{-}if}$ is considered as the lower limit for dense c-Zr_3N_4.

In order to obtain the thermal expansion coefficient of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$, its XRD powder patterns were collected on heating in air to 873 K. The observed nonlinear temperature dependence of the lattice parameter of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ (Fig. 3) was fitted with a third order polynomial function: $a(T) = 674.6 + 8.422 \times 10^{-6} T^2 - 2.205 \times 10^{-9} T^3$ [pm]. This dependence fulfils the boundary condition for the thermal expansion coefficient (lim $\alpha(T) = 0$ for $T \to 0$) and the tendency of $\alpha(T)$ to a constant value at high temperatures [31]. Applying this result we derived the linear thermal expansion coefficient $\alpha(T)$ defined as $\alpha(T) = (\partial a(T)/\partial T)/a(T)$ (Fig. 3). It can be seen from Fig. 3 that $\alpha(T)$ increases from 6.6×10^{-6} K^{-1} to 14.2×10^{-6} K^{-1} in the investigated temperature region and is about twice as large as those of δ-ZrN [32–34] and o-Zr_3N_4 [5] at 900 K. Such a high $\alpha(T)$ value of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ can be explained by a less symmetric interatomic potential in c-Zr_3N_4 due to higher atomic coordinations when compared with δ-ZrN and o-Zr_3N_4. It should be also mentioned that, similar to o-Zr_3N_4 and zirconium oxynitrides [35], c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ starts to oxidise in air above 773 K. The main oxidation product was found to be γ-Zr_2ON_2 [36] which further oxidises to monoclinic ZrO_2.

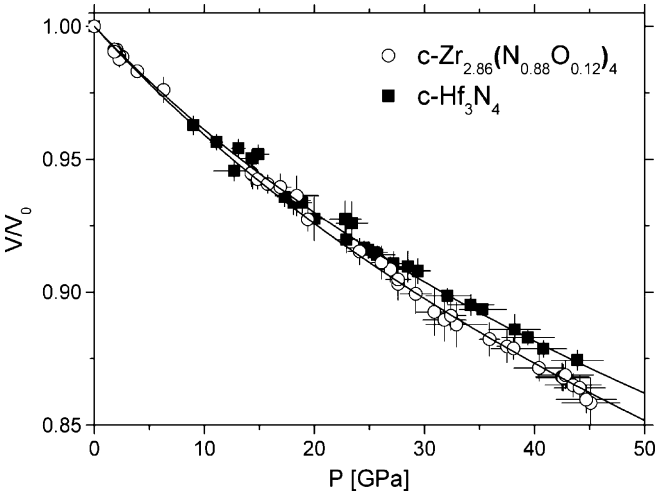

Fig. 2. Pressure dependences of V/V_0 of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ (open circles) and c-Hf_3N_4 (solid squares) measured at RT. Solid lines represent the least-squares fit of the third-order Birch-Murnaghan EOS to the experimental data. The fits yielded $B_0 = 219(13)$ GPa, $B_0' = 4.4(10)$ and $B_0 = 227(7)$ GPa, $B_0' = 5.3(6)$ for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ and c-Hf_3N_4, respectively.

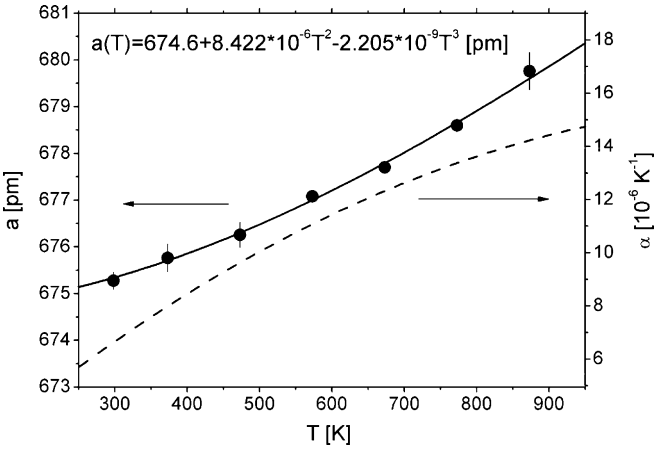

Fig. 3. Thermal expansion data for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$: Lattice parameter, $a(T)$, measured at elevated temperatures (solid circles) and fitted by a third order polynomial function (solid line). Linear thermal expansion coefficient, α, as a function of temperature (dashed line).

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