

Synthesis of Hf-C-N ceramics by spark plasma sintering

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Abstract. We obtained the Sample by the spark plasma sintering (SPS) of commercially available HfC and HfN powders. The identification of obtained material was carried out by the X-ray diffraction and the Raman spectroscopy. The solid solution of previous material was confirmed. However oxide phase excreted while sintering presumably due to oxygen impurities of used commercially powders.

1 Introduction

The reasons of the extreme thermal stability of the most refractory compound Ta_4HfC_5 (the melting point ~ 3990 C) were considered in detail in [1]. The search result for the isostructural analogs of this compound in the Ta-Hf-C-N-B system by the numerical simulation method was the assumption that the melting point of the non-stoichiometric compound $Hf_{0.53}C_{0.27}N_{0.2}$ is higher up to 200 C. Until now, this assumption has not been confirmed experimentally. Therefore, that is the ultimate goal of the authors. The first task on the way to this goal is to obtain Hafnium Carbonitride.

Hafnium Carbide and Nitride have complete mutual solubility and form a solid solutions continuous series [2-6]. The extensive work on obtaining compounds in the Hf-C-N-O system with different stoichiometry by the vacuum hot pressing method from powders HfC, HfN, HfO₂, Hf, and C has been carried out for a long ago [2]. The preparation of Hafnium Carbonitride stoichiometric solid solutions mainly occurred during the HfC and HfN powders sintering while the maximum temperature was ≥ 2300 C for 10-30 min. According to [2], the stoichiometric compound $HfC_{0.58}N_{0.42}$ possesses extreme hardness properties with the ratio $N/C \approx 0.72$ close to the ratio of these elements in the proposed in [1] compound $Hf_{0.53}C_{0.27}N_{0.2}$ – $N/C \approx 0.74$. Apparently, such a ratio of the elements in the nonmetallic sublattice best satisfies the revealed in [1] exceptional crystal lattice stability reasons. Therefore, in this work we used the simplest and the closest relation $HfN/HfC = 3/4 = 0.75$.

The modern promising method for creating refractory materials is the Spark Plasma Sintering (SPS) (used in this paper). Its advantages over the more classical hot pressing method were demonstrated in [7] for the Ta-Hf-C system. However, the publications about the SPS obtaining materials in the Hf-C-N system are absent. Therefore, the problem of

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obtaining Hafnium Carbonitride by the SPS method from HfC and HfN powders was solved in this study.

2 Materials and methods

We used the commercial HfC and HfN powders (Compleks, Russia) (“HfC” and “HfN” respectively in text). The powders mixture (assuming the molar ratio HfN/HfC = 3/4), was prepared by the planetary mill grinding Pulverisette 6 (Fritsch, Germany) in 6 cycles of 10 min. with a break of 5 min. at 650 rpm. The ZrO₂ poulder and balls (6, Ø 1 cm) were used while material loading was ~30 g. A homogenization was the goal so the milling parameters were not specially selected. The mixture (12.12 g) was placed in a graphite crucible and sintered according to the programmed regime in the vacuum (6 Pa) in the SPS-515S (Dr. Sinter-LABTM, Japan) to obtain the Sample. The chosen regime based on the related topics [2, 8, 9] and the team experience (for example, [10-13]). The average heating rate was 100 C/min, the maximum sintering temperature was 2100 C, the holding time at a maximum temperature of 5 min, and the pressing pressure was constant throughout the process and was 50.4 MPa. The test surface of the Sample was first manually cleaned off graphite paper used while sintering by various grain sizes corundum sandpapers (P100-P2000 according to ISO-6344) and then ground and polished on the machine MECATECH 234 (PRESI, France) with pre-hot pressing in acrylic resin on the machine MECAPRESS 3 (PRESI, France). The powders and the Sample were investigated on the metallographic microscope Eclipse MA200 (Nikon, Japan). Their phase compositions were identified by the X-ray diffraction carried out on the multipurpose X-ray diffractometer D8 Advance (Bruker, Germany) using Cu K_α duplet and from the Raman specters obtained on the optical microscope with the Raman spectrometer Morphologi G3SE-ID (Malvern, UK) using Ar-laser wavelength 514.5 nm.

3 Results and discussions

The XRD of the Sample and powders are presented on Fig. 1. The double scattering angles investigated range is 5-90° but Fig.1 demonstrates only peak-containing sections.

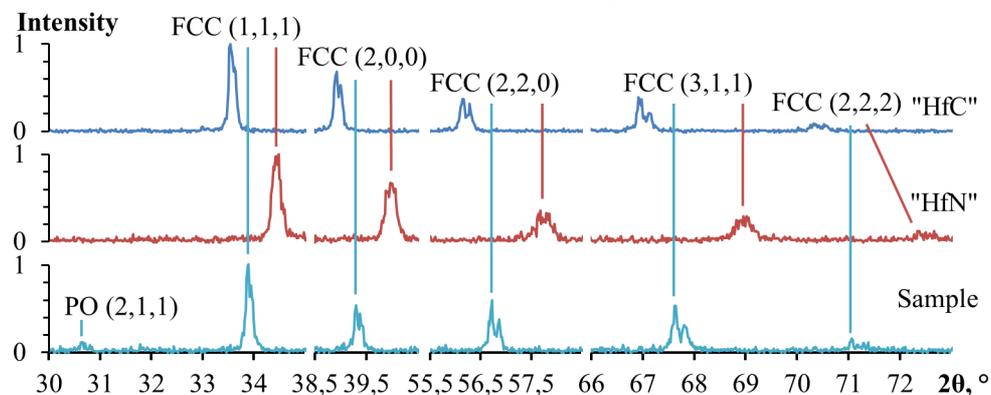


Fig 1. The XRD of powders (“HfC” and “HfN”) and the test surface of the Sample.

The Sample peaks lay between the peaks of “HfC” and “HfN” – that proves the solid solution obtaining. The XRD indexing uniquely identifies the face-centered cubic (FCC) lattice. The Cu K_α duplet reflexes are clearly distinguishable. The precise positioning of the peaks further the second is difficult so the lattice constants were calculated only from first

and second reflexes: "HfC" – 4.625 ± 0.002 Å; "HfN" – 4.506 ± 0.004 Å; Sample – 4.582 ± 0.003 Å. The lattice constants of "HfC" and "HfN" are less than the standards: HfC – 4.638 Å [14]; HfN – 4.525 Å [15]. This is typical for defective structures – for example, with some oxygen impurities. If the linear dependence between a lattice constant and electronegativity is assumed then the lattice constant of fictive phase 'HfO' will be estimated (~ 4.416 Å) as well as (adopting Vegard's rule) the share of the substituting oxygen: $\sim 6\%$ for "HfC" and $\sim 18\%$ for "HfN".

According to optical microscopy (Fig. 2.a), the grain size and coarse pore fraction correspond to the dispersion of the powders (not presented) – $10\text{-}20$ μ . The fine pores fraction ($\sim 1\text{-}3$ μ), apparently, is the intrinsic porosity of the sintered particles, which is typical for self-propagating high-temperature synthesis of powders. Two phases are clearly visible on the photomicrograph (Fig. 2.a). The light main phase corresponds to FCC peaks (Fig. 1). The dark phase can be correlated only with a weak peak close to the reflex (211) Primitive orthorhombic (PO) HfO₂ [17]. The dark phase identification was carried out by Raman spectroscopy (Fig. 2.b).

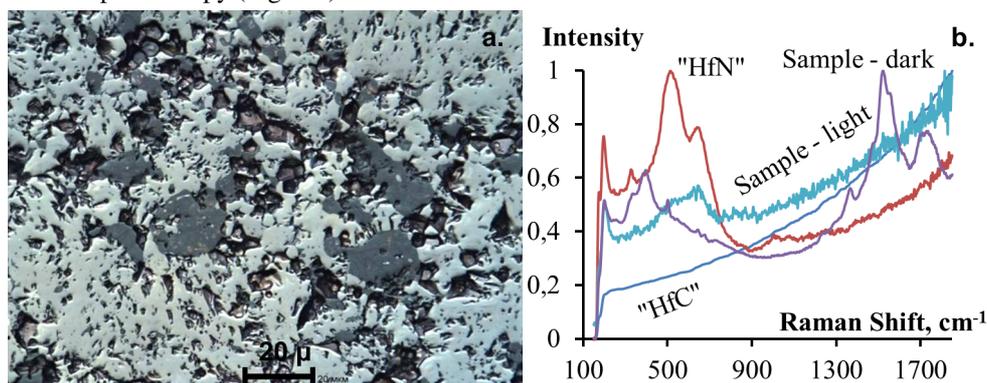


Fig 2. a. The Sample test surface microphoto. b. The Raman spectra for powders and Sample phases.

The porosity preservation indicates the sintering without significant softening which is fully corresponds to a low sintering temperature (~ 2100 C) in comparison with the melting points of HfC (~ 3890 C) and HfN (~ 3380 C). The formation of a new solid solution phase occurred during the mutual diffusion of C and N. It required lower temperatures in comparison with the SPS production of Ta₄HfC₅ [8, 9] (≥ 2350 C), which may be explained by the facilitated diffusion of C and N due to their smaller masses and sizes (v.s. Ta and Hf).

"HfC" and the main (light) phase do not have a pronounced spectrum in the investigated range of Raman shifts. The "HfN" lines correspond to HfN with a defective structure [18], which was also revealed by Fig.1. The implicitly expressed broad peak of the light phase ($\sim 400\text{-}750$ cm^{-1}) can be associated with the HfN lines. The Raman spectrum of the dark phase corresponds to HfO₂ [19]. Deviations are explainable by the presence of defects.

3 Conclusions

This study task was to obtain Hafnium Carbonitride by the SPS. The oxygen admixture in the used powders led to the additional oxide phase separation. However, there is no reason to believe that oxygen plays a key role in sintering. Thus, the posed task can be considered as solved. The material was obtained at lower temperatures (~ 2100 C) and holding time (5 min) than used in more traditional methods [2-4] (≥ 2300 C, ≥ 10 min). Further, the SPS method will allow to obtain the qualitative Hafnium Carbonitride ceramic materials by

more carefully selecting the sintered powders and preparing samples for testing the hypothesis about more refractory compounds in the Hf-C-N system than Ta₄HfC₅.

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