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Synthesis and characterization of hafnium carbide fine powders

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Abstract

Hafnium carbide powder was synthesized by sol–gel polycondensation of hafnium chloride with citric acid. The starting materials were dissolved in water and mixed homogeneously on a hot plate until precursor gel was formed. Pyrolysis of this gel resulted in monoclinic hafnia which after subsequent heat treatment transformed into hafnium carbide. The obtained materials were analyzed by means of X-ray diffraction and scanning electron microscopy. The results showed that the obtained carbide powders were composed of nearly equiaxed particles with narrow size distribution. Characterization by nitrogen adsorption showed that the obtained powders were micro- and mesoporous materials with high specific surface area.

Keywords: A. Powders: chemical preparation; B. Electron microscopy; B. X-ray methods; Hafnium carbide

1. Introduction

Hafnium carbide (HfC) belongs to so-called “hard metals”. These materials are carbides of transition metals of groups IV–VI in the periodic table. HfC is a promising candidate for extremely high-temperature applications owing to its high melting point (> 3900 °C), high hardness and elastic modulus and good resistance to chemical attack [1–6]. In view of these properties, HfC is an attractive material for applications in the fields such as nuclear rocket propulsion, nuclear reactors, space air craft industry and thermal-field emitters. Since the natural sources of hafnium carbide do not exist, HfC-based ceramic powders have been exclusively obtained from the synthetic materials. As the majority of carbide ceramics are normally made by sintering of powders, their properties depend to a great extent on the quality of the starting powders.

Hafnium carbide can be prepared by heating almost any source of hafnium metal and carbon at high temperatures [7]. Several different synthesis routes for HfC powder are available. Some of them are solid combustion synthesis by direct combination of the elements at elevated temperatures, carbothermal reduction of metal oxide compounds, vapor phase synthesis, sol–gel route, laser induced reactions, plasma-chemical synthesis and pyrolysis of metal organic compounds [8,9].

The synthesis of pure HfC powder is the first prerequisite for fabrication of dense HfC ceramics. Although the quality and performance of ceramic components are important, the cost of mass production is the key factor in the commercialization of HfC ceramics. Thus it is essential to develop technique for synthesis of ceramic powder with reasonable low production cost. With this point of view many of the above mentioned fabrication methods would never meet the commercialization.

HfC powder is usually synthesized by reaction between carbon and some source of hafnium such as pure hafnium (Hf), metal hydride (HfH_2) or metal oxide (HfO_2) [9,10]. HfO_2 is considered to be the most suitable raw material for HfC synthesis as it is much cheaper and thermodynamically more stable than Hf and HfH_2. The carbothermal reduction method is based on reaction [11].

$$HfO_2 + 3C = HfC + 2CO \qquad (1)$$

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Even though the formation of final product is more complex than Eq. (1), this procedure offers the possibility of an economical production route. Therefore, studies on low-temperature synthesis and low-cost precursors are among the main emphases of ongoing research effort.

In this paper, the possibility to manufacture HfC powder using hafnium chloride ($HfCl_4$) and citric acid as a source of hafnium and carbon, respectively was studied. According to the authors knowledge, no work about the synthesis of HfC from these precursors has been yet performed.

2. Experimental

Commercial $HfCl_4$ was used as a source of hafnium whereas citric acid monohydrate $[C(OH)(COOH)(CH_2COOH)_2 \cdot H_2O]$ was used as carbon source. The precursor mixture was prepared by wet chemical method. The appropriate amounts of $HfCl_4$ and citric acid were progressively dissolved in distilled water. The pH value of the water solution was adjusted to 2–3 by adding a small amount of ammonia solution (25%). The water solution was heated to 300 °C on a hot plate with continuous stirring in order to remove water. The solution viscosity increased due to formation of precursor gel. The gel was pyrolyzed at 800 °C in argon flow for 1 h. The precursor powder was compacted (10 mm diameter) at a pressure of 50 MPa using a uniaxial hydraulic press. The bodies were heated (annealed) at temperatures between 1000 °C and 1600 °C with controlled argon flow. The annealed bodies were afterwards crushed into powder.

Crystal structure was identified by X-ray diffraction (XRD) using filtered Cu Kα radiation (Siemens D5000). The angular correction was done before measurement by high quality Si standard. The morphology of obtained powders was analyzed by means of scanning electron microscopy (SEM) using JEOL 6300F microscope at 3 kV accelerating voltage. Adsorption and desorption of N_2 on samples obtained at different temperatures were measured at −196 °C, using the gravimetric McBain method. The specific surface area and pore size distribution were calculated from the adsorption and desorption isotherms [12]. Pore size distribution was estimated by applying BJH method [13,14] to the desorption branch of isotherms.

3. Results and discussions

XRD patterns of precursor powder pyrolyzed at 800 °C and powders obtained by subsequent annealing of pyrolyzed powder at different temperatures are presented in Fig. 1. As figure shows diffraction lines of pyrolized gel (a) are quite diffuse which makes the identification of some atomic planes almost impossible. However, the position of reflections corresponds to monoclinic hafnia (HfO_2). Unlike pyrolyzed powder, the annealed powders exhibit clear diffraction lines which are a result of an increase in crystalline size. As can be seen, temperature of 1000 °C was sufficiently high to obtain crystallized powder of monoclinic hafnia (b). It is worth noting that carbon peaks do not appear which indicates that the present carbon is in an amorphous state. It is believed that the amorphous carbon reacts with HfO_2 and forms HfC. This conclusion is based on fact that small amount of HfC ($2\theta = 33.6°$; 38.8°; 55.9° and 66.7°) is detected even at 1000 °C. The comparatively low reaction temperature is attributed to an intimate, atomic level, mixing of Hf and carbon which is achieved by gelation of water solution of the precursors. This intimate mixing provides better contact between Hf and carbon atoms and shortens the diffusion path. Semi-quantitive analysis done by Power Cell Program showed that sample annealed at 1000 °C consists of 98% of monoclinic hafnia, 0.6% of cubic hafnia and 1.4% of hafnium carbide. As expected, the increase in annealing temperature increases the amount of HfC. Fig. 1 indicates that HfC is the principal phase in sample annealed at 1200 °C (c). Beside HfC (~79%) monoclinic HfO_2 (18%) and cubic HfO_2 (3%) were also detected. Further increase in annealing temperature to 1400 °C (d) increased the fraction of HfC to approximately 92%. Finally, the annealing at 1600 °C resulted in almost pure HfC powder with small amount of cubic HfO_2 (e). Again, the crystal carbon was not detected even at temperature as high as 1600 °C indicating that amorphous carbon reacts with HfO_2 to form HfC.

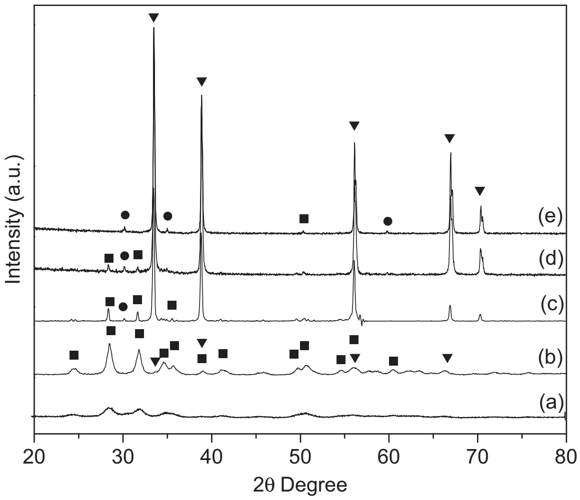

Fig. 1. Effect of temperature on phase evolution during one-hour annealing of gel pyrolyzed at 800 °C (a); and pirolyzed gel annealed at 1000 °C (b); 1200 °C (c); 1400 °C (d) and 1600 °C (e). Monoclinic hafnia-■, cubic hafnia-● and hafnium carbide-▼.

Morphologies of powders obtained by annealing of pyrolyzed gel at different temperatures are presented in Fig. 2. Fig. 2(a) reveals that powder annealed at 1000 °C is cemented in a form of agglomerated lumps. Further increase in annealing temperature completely changes the morphology of the powder. Fig. 2(b) shows that agglomerates in sample annealed at 1200 °C are broken into smaller pieces but still without clear crystal forms. This change in morphology

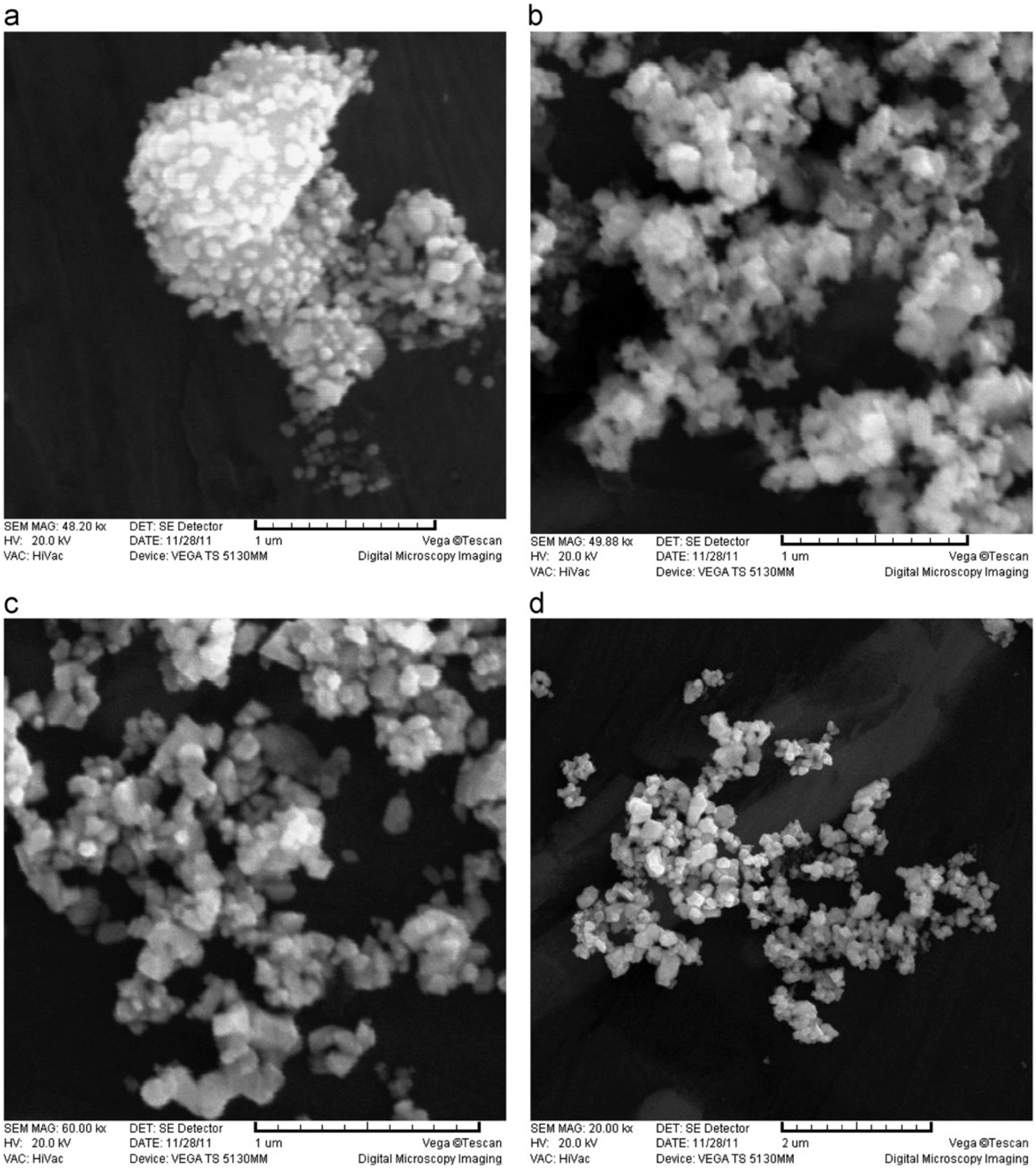

Fig. 2. SEM images of powders annealed at (a) 1000 °C; (b) 1200 °C; (c) 1400 °C and (d) 1600 °C for 1 h.

might be related to intensive transformation of HfO_2 to HfC. As mentioned, the increase in temperature from 1000 to 1200 °C was followed by an increase in amount of HfC from 1.4% to 79%. Unlike powder annealed at 1200 °C, powders annealed at higher temperatures such as 1400 °C and 1600 °C consist of well defined, nearly equiaxed, particles with narrow size distribution (Figs. 2c and d). The change in morphology can be ascribed to high annealing temperature which provides fast diffusion necessary for crystallite growth. It can be roughly estimated that the particle size of sample annealed at 1600 °C lies in the range of 100–200 nm.

Nitrogen adsorption and desorption isotherms for samples annealed at different temperatures are shown in Fig. 3(a). The isotherms are given as the amount of N_2 adsorbed as function of relative pressure at -196 °C. The isotherms for HfC sample obtained at 1600 °C are not presented since the specific surface area and therefore adsorbed amount of N_2 was very low, below the detection limit of the instrument. According to the IUPAC classification [13,14] all isotherms are of type IV. It is interesting to note that the type of hysteresis loop is different for each sample. The shape of hysteresis loop for powder annealed at 1000 °C is of type H2 which indicates a poorly defined shape of pores. Powder sample annealed at 1200 °C has H3 type of hysteresis loop which is observed with non-rigid aggregates of plate-like particles giving rise to

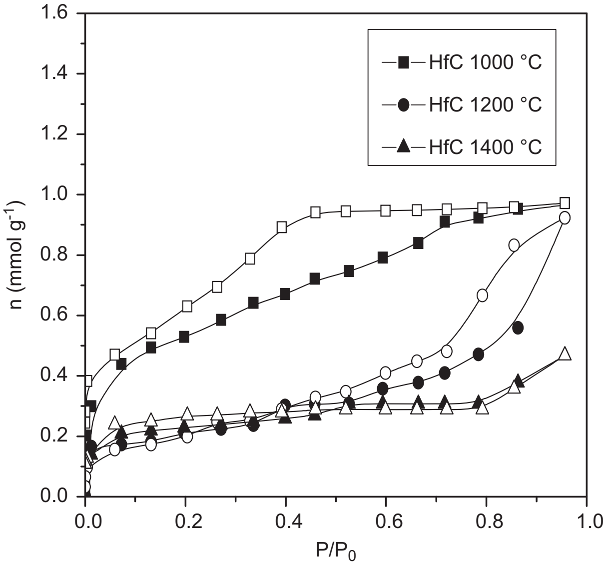

Fig. 3. Nitrogen adsorption isotherms, as the amount of N_2 adsorbed as function of relative pressure for samples obtained at different temperatures. Solid symbols-adsorption, open symbols-desorption.

slit-shaped pores. Finally, powder sample annealed at 1400 °C has H4 type of hysteresis loop which is often associated with narrow slit pores, including micropores. The formation of slit-shaped pores is quite expected since well defined particles of HfC were formed after annealing at high temperature such as 1400 °C.

Specific surface areas calculated by BET equation for samples obtained at 1000 °, 1200 ° and 1400 °C lie within 42–17 m^2g^{-1}, respectively. As Fig. 3 shows the largest drop in specific surface (amount of adsorbed N_2) occurs when annealing temperature increases from 1000 to 1200 °C. It implies that the agglomerated lumps of HfO_2 which were found in sample annealed at 1000 °C (Fig. 2a) are fairly porous. It is also believed that these lumps contain amorphous carbon which reacts with HfO_2 to form HfC. As mentioned before HfC is the dominant phase in sample annealed at 1200 °C. Although the formation of HfC is followed by the breakage of the lumps (Fig. 2b) there is no increase in specific surface. This points out that the newly formed agglomerates of HfC are less porous due to increased diffusion at 1200 °C. Further support to this conclusion was found in pore size distribution (PSD) of samples annealed at different temperatures which is given in Fig. 4. As figure shows, the sample annealed at 1000 °C is mostly microporous whereas the sample annealed at 1200 °C is completely mesoporous. This finding indicates that the relatively large (> 2 μm) lumps in sample annealed at 1000 °C contains a large number of small pores, so called micropores (< 2 nm) which are smaller than mesopores (2–50 nm). Furthermore, besides mesoporosity, the sample annealed at 1400 °C possesses developed microporosity as well. The formation of small pores (micropores) in sample annealed 1400 °C can be ascribed to improved diffusion which helps shrinkage of mesopores.

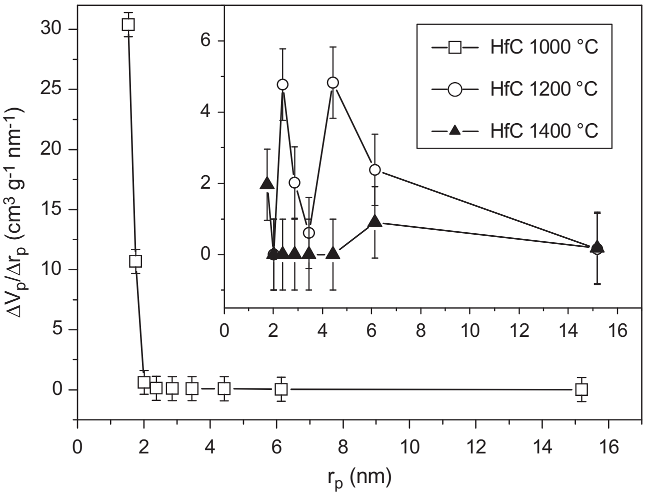

Fig. 4. Pore size distribution (PSD) for samples obtained at different temperatures with experimental error bars. Inserted diagram shows results for samples obtained at 1200 and 1400 °C.

4. Conclusions

A carbothermal method was used to produce hafnium carbide from $HfCl_4$ and citric acid. Hafnium carbide formation started at 1000 °C. The comparatively low reaction temperature is attributed to an intimate, atomic level, mixing of Hf and carbon which is achieved by gelation of water solution of the precursors. Increase in temperature resulted in an increase in volume fraction of formed hafnium carbide. Nearly pure hafnium carbide (~97%) was obtained at 1600 °C. Hafnium carbide grows in a very well developed habitus of crystals in range of 100–200 nm. In order to obtain powders as pure as possible, it is necessary to perform heat treatment with different soaking time and to prepare precursors with a higher C/Hf ratio (> 3).

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