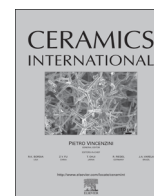




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# Synthesis of ultra-fine hafnium carbide powders combining the methods of liquid precursor conversion and plasma activated sintering

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## ABSTRACT

Ultra-fine hafnium carbide (HfC) powders were synthesized using a novel method combining liquid precursor conversion and plasma activated sintering (PAS). Solution-based processing was used to achieve a fine-scale mixing of the reactants, and further treatment by PAS allowed fast formation of HfC. We investigated the effect of the type of acid used during the liquid precursor conversion on the synthesized powders, where mixtures were prepared using salicylic acid, citric acid, or a combination of these. The results show that pure HfC powders (with an average particle sizes of 350 nm) were obtained at a relatively low temperature (1550 °C) using a  $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$  precursor with the mixed acids. The oxygen content of the synthesized powders was only 0.97 wt%. The type of acid had a significant effect on the synthesis product. When using only citric acid, the temperature required to produce pure hafnium carbide increased to 1700 °C. In the case of a salicylic acid precursor, pure HfC was not obtained, even at a synthesis temperature of 1700 °C.

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## 1. Introduction

Hafnium carbide has a face-centered cubic NaCl crystal structure [1]. The hafnium carbide structure exhibits both metallic and covalent bonding, which leads to favorable physical and chemical properties, such as high hardness, high strength, and high melting point [2]. Hence, hafnium carbide has applications in the field of cutting tools and mold field due to its high hardness [3], and in the field of rocket nozzles due to its high modulus of elasticity, high thermal and electrical conductivities, and high melting point.

Hafnium carbide powders are usually synthesized by reacting a carbon precursor with a source of hafnium, such as pure metallic hafnium (Hf), a metal hydride ( $\text{HfH}_2$ ) or a metal oxide ( $\text{HfO}_2$ ) [4]. In most cases of carbide synthesis reactions, coarse precursor powders are mixed together and treated at high temperatures, leading to metal carbide products with relatively large particle sizes [5]. Liquid precursor conversion methods are a promising alternative due to low production costs and the simplicity of the processing and equipment [6]. Such methods can be used to synthesize HfC powders at lower temperatures. Sacks et al. synthesized HfC powders

(< 1500 °C) using hafnium isopropoxide, and polyhydric alcohol or phenol–formaldehyde resin as the carbon source. The HfC products still contained some oxygen and hence high temperatures and long reaction times were required to complete the reactions. Wang et al. prepared HfC powders at 1500 °C using hafnium oxychloride, hydrochloric acid, nitrate, propanol, isopropanol, ethanol and acetylacetone, but the products still contained some  $\text{HfO}_2$  particles [7]. Dolle et al. prepared ZrC powders using zirconium n-propoxide and saccharose, which resulted in highly agglomerated products [8]. Yan et al. prepared ZrC powders using zirconium oxychloride octahydrate, specific ligands and phenolic resin, however, there were problems with agglomeration and residual carbon.

Spark plasma sintering (SPS) has been shown to produce powders with minimal grain growth due to the fast heating and cooling rates during processing [9].  $\text{HfB}_2$  powder was prepared using SPS via solid-state reaction of  $\text{HfO}_2$ ,  $\text{B}_4\text{C}$ , and C [10]. The as-synthesized powders agglomerated because the mixed precursor powders were relatively coarse [11].

In the present study, a novel method combining liquid precursor conversion with spark plasma sintering is proposed. We fabricated ultrafine HfC powders using hafnium dichloride oxide octahydrate ( $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ ) and a mixture of salicylic and citric acids as precursors.

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## 2. Material and methods

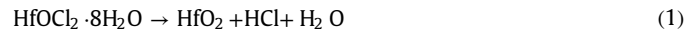
The precursor material was prepared using hafnium dichloride oxide octahydrate (purity > 98%, Zr < 1.5%, Alfa), salicylic acid (AR, Sinopharm) and citric acid (AR, Sinopharm). Firstly, a certain amount of  $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$  and salicylic acid was dissolved in ethanol. The solution was refluxed at 75 °C for 1 h, then stirred at room temperature for 1 h in order to form a complex-based solution. Next, a certain amount of citric acid was added and the mixture was stirred at room temperature for another hour. Control samples were prepared using the same method with the  $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$  precursor and only one of the acids (salicylic acid or citric acid). All of the solutions were dried at 65 °C using a rotary evaporator to obtain powder samples, which were then ground before being pyrolyzed at 800 °C (4 °C/min heating/cooling rate) in a tube furnace for 30 min under an argon atmosphere. Then, the pyrolysis products were milled using a planetary ball mill to break up any aggregates. Finally, the powders were placed in graphite crucibles for reduction processing in the PAS system (ED-PAS-111, ELENX, Japan). These experiments were carried out in an argon atmosphere with a heating rate of 300 °C/min at temperature ranging from 600 °C to 1550 °C.

The thermodynamics of the HfC production process were measured by differential thermal analysis (TG–DSC, Netzsch STA449F3, Germany) in an argon atmosphere with a heating rate of 10 °C/min. The phase compositions of the powders were examined by X-ray diffraction (XRD) using filtered Cu-K $\alpha$  radiation with the incidence beam angle of 2° in the range of 10–90° (step: 0.02°, step time 1 s). The phases present were analysed by means of the software Search Match. Rietveld refinement were completed using the software Maud. Scanning electron microscopy (SEM, Hitachi S-3400) and field

emission transmission electron microscopy (FETEM, JEM2100F) were used to analyze the morphology of the obtained powders. The remaining oxygen content in the powders was detected using an oxygen analyzer (TC-600, Leco). The particle size distribution of the produced powders was determined using a particle size analyzer (Mastersizer2000). Fourier transform infrared spectra (Nicolet6700) of the hafnium carbide powders were obtained between 4000 and 400  $\text{cm}^{-1}$ .

## 3. Results and discussion

Fig. 1 shows the TG–DSC curves of the dried powders prepared by the three different precursor compositions. For the powder produced using two acids (A), TG analysis shows that the main weight loss occurred below 600 °C due to the liberation of bonded water and the decomposition of the salicylic and citric acids. The total weight loss was about 32.5 wt%. The endothermic peak at 207 °C may be due to the evaporation of structural water and the hydrolysis of  $\text{HfOCl}_2$  (there was observed a small amount of hafnium oxide nucleation at 180 °C (Fig. 2)). A possible reaction mechanism is:



The endothermic peak at 460 °C may be due to the decomposition of the acids because a large degree of weight loss is observed at this temperature and there are no other components in sufficient quantity to cause such a large change. It is known that there are four crystalline forms of hafnium oxide (monoclinic, orthogon, tetragonal, and cubic), and the stability of these crystalline forms vary at different temperatures. Hence, the endothermic

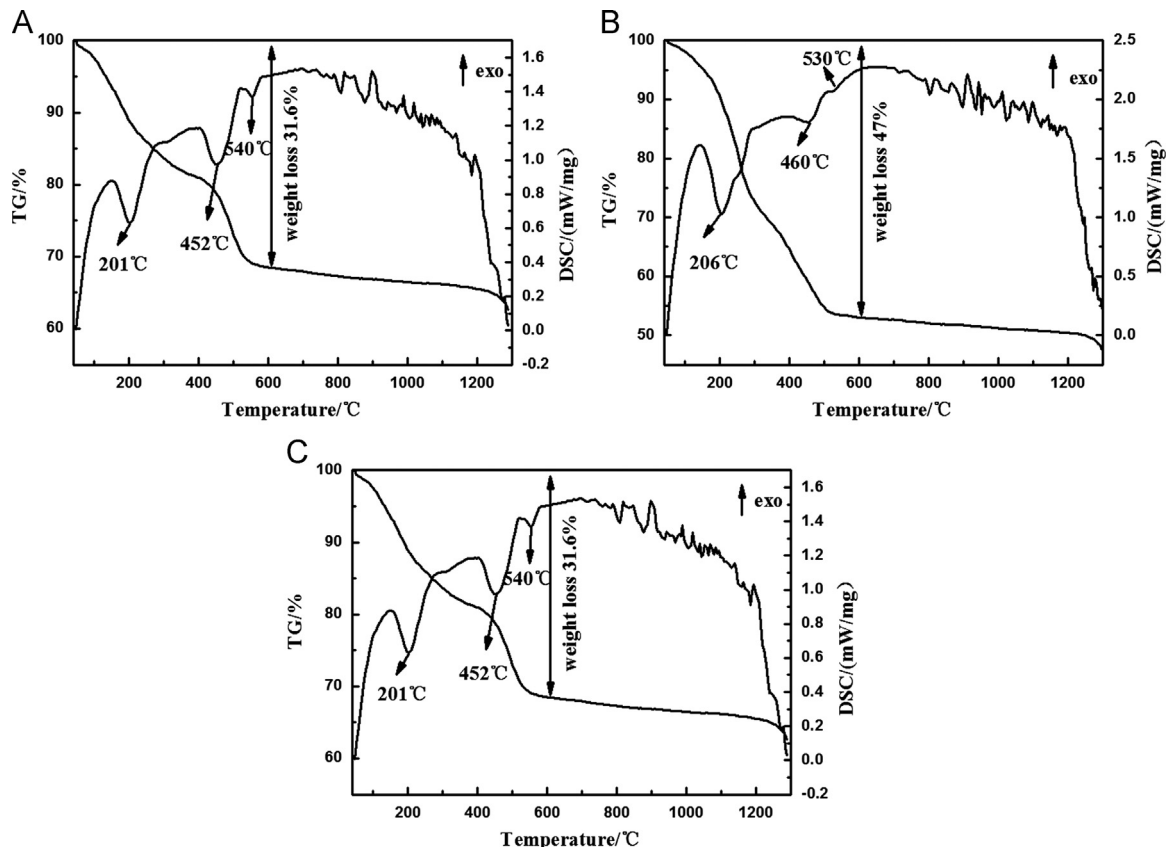


Fig. 1. TG–DSC curves of the different precursor powders: A. Hafnium dichloride oxide–salicylic acid and citric acid; B. Hafnium dichloride oxide–citric acid; C. Hafnium dichloride oxide–salicylic acid.

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