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Preparation of Fused Hafnium (IV) Carbide from Mechanochemically Synthesized Hf/C Composite

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Abstract

Mechanochemical preparation of nanoscale hafnium (IV) carbide was explored. It was demonstrated that the Hf/C mechanocomposite with a wide particle-size distribution was formed in the first step. Fused hafnium (IV) carbide was produced from nanoscale hafnium (IV) carbide and the hafnium/carbon mechanocomposite by treatment with high-intensity photon flux. According to research results, the mechanocomposite is more preferable and may be used as a precursor to make products of fused hafnium (IV) carbide using additive technologies.

Key words: mechanochemical synthesis, hafnium, carbon, Hf/C mechanocomposite, nanoscale and fused hafnium carbide, photon flux irradiation

INTRODUCTION

Due to elevated thermal stability (the melting point of hafnium (IV) carbide is identified as (3965±50) °C [1]), high hardness, chemical stability, low vapour pressure, and good thermal shock resistance, hafnium carbide is a material required for modern airspace engineering.

There are known industrial methods of preparation of hafnium (IV) carbide [2]: 1) reduction of hafnium (IV) oxide by carbon at 1200 °C in vacuum and 2000 °C in hydrogen atmosphere, 2) deposition of hafnium (IV) chloride from gas phase followed by carbon reduction, 3) self-propagating high-temperature synthesis.

The main drawbacks of industrial methods of synthesis of hafnium (IV) carbide are the impossibility to prepare a superfine material with the stoichiometric composition, high temperatures, the multi-step nature and duration of synthetic processes, and environmental pollution.

In the 1990s, many researchers began using the mechanical activation method to synthesize carbides [3–11]. The resulting powders had 5–100 nm particle size; however, the completion time of synthesis reaction was not less than 30 min, and in some cases, it reached tens of hours. Hafnium (IV) carbide has high hardness, due to which there is contamination of mechanochemical reaction product with materials from drums and grinding bodies.

Hafnium (IV) carbide products are traditionally produced by powder metallurgy technique. As carbides are poorly pressed due to high hardness, sintered products have high porosity. In order to reduce porosity, hot pressing [12, 13] and spark plasma [14, 15] are used. Most of the modern research papers are devoted to methods for producing hafnium carbide in a highly dispersed state, which allows reducing porosity and improving powder sintering.

The purpose of the research work was to explore the stepwise nature of the formation of the Hf/C composite and nanoscale hafnium (IV) carbide to produce fused hafnium (IV) carbide therefrom.

EXPERIMENTAL

For the purpose of investigating the mechanism of mechanochemical synthesis of the Hf/C composite and hafnium (IV) carbide, the research work used HFM Hf and PM-15 lamp soot powders. Ultrafine Hf/C mechanocomposite and nanoscale hafnium (IV) carbide were produced in an AGO-2 high-energy ball planetary mill with water cooling under argon. The volume of the drum is 250 cm^3; the diameter of the balls is 5 mm; the mass of the balls is 200 g; the sample mass is 10 g and the rotation speed of the drums around the common axis is ~1000 rpm [16].

Experiments on producing fused hafnium (IV) carbide from mechanochemically synthesized hafnium (IV) carbide and the Hf/C mechanocomposite used a pulsed-periodic CO_2 laser system, such as a generator-amplifier with a wavelength of ~10.6 μm [17]. The system operated in a continuous mode with a power of ~1.0 kW during experiments. The laser beam was focused on a sample from a hafnium/carbon mechanocomposite powder (or a hafnium carbide powder) into an area with a diameter of ~3.0 mm (at a level of ~0.8 power) with intensity distribution close to Gaussian and ensured ~40 kW/cm^2 irradiation intensity on the beam axis. The irradiation spot over the sample was moved along the Archimedes spiral with a step of 1 mm at an average rate of 5.4 mm/s in the protective medium of atmospheric pressure argon.

Diffraction investigations of the structure of the resulting samples were carried out using hard (quantum energy of 33.7 keV) synchrotron radiation (SR) at the station of the 4th SR channel of the VEPP-3 storage ring of the Siberian centre of synchrotron and terahertz radiation [18]. Powder samples were placed in a thin layer in a ring holder; the survey was carried out in transmission geometry, the primary beam size of 0.4 × 0.4 mm. Diffracted radiation was recorded using a mar345 two-coordinate detector. The exposure time was 10 min. The data acquired from the two-coordinate detector were integrated in all directions, and phase analysis of samples was car-

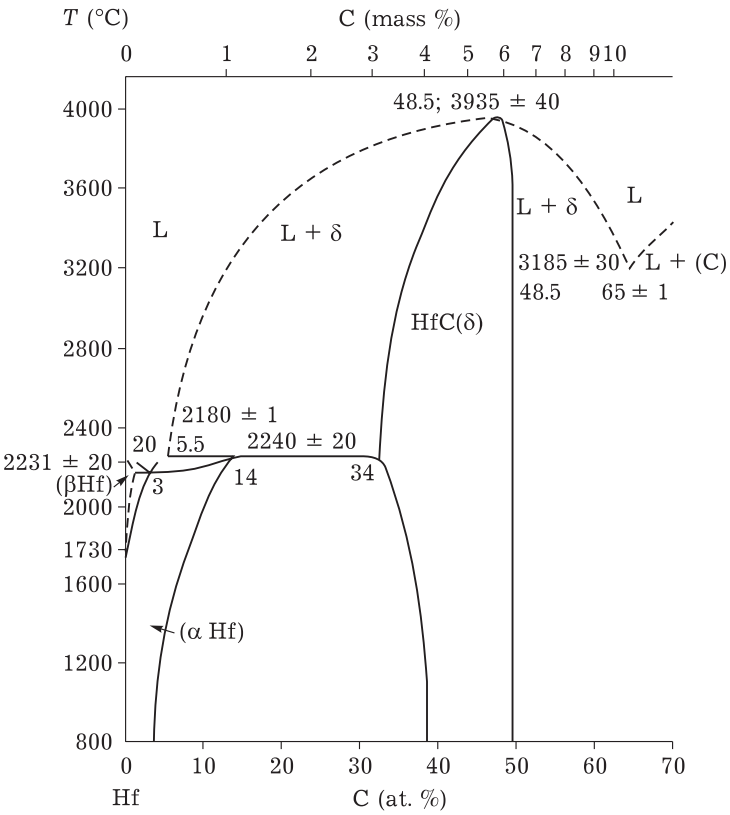

Fig. 1. Phase diagram of the Hf–C system [19].

ried out relying on the resulting X-ray diffraction patterns.

The certified accuracy of the device in determining interplanar distances for standard samples was not less than $4 \cdot 10^{-4}$ Å.

Microscopic investigations by transmission electron microscopy (TEM) were performed using a JEM-2010 microscope with a resolution of 0.14 nm and an accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

A single HfC compound with a wide homogeneity range (~15 at. %) is registered in the Hf–C system [19] (Fig. 1).

Hafnium carbide has the FCC NaCl type structure. According to electron microscopy data, the initial hafnium powder is comprised of inhomogeneously-shaped micron-size particles, with a relatively smooth surface.

As the melting point of hafnium (~2230 °C [19]) is lower than the adiabatic temperature of the interaction of Hf and carbon (~3630 °C), whereas the enthalpy formation of hafnium (IV) carbide is high, $\Delta_f H^0_{298}$ (HfC) = −227.09 kJ [20] (−218.3 kJ [21]), the mechanochemical interaction in the Hf–C system takes place with participation of liquid hafnium. According to X-ray phase analysis data (Fig. 2), mechanical activation (MA) of a mixture of Hf and C for 10 s and 2 min leads to the formation of the Hf/C mechanocomposite only. There are intensity reduction and the broadening of hafnium reflections in X-ray diffraction

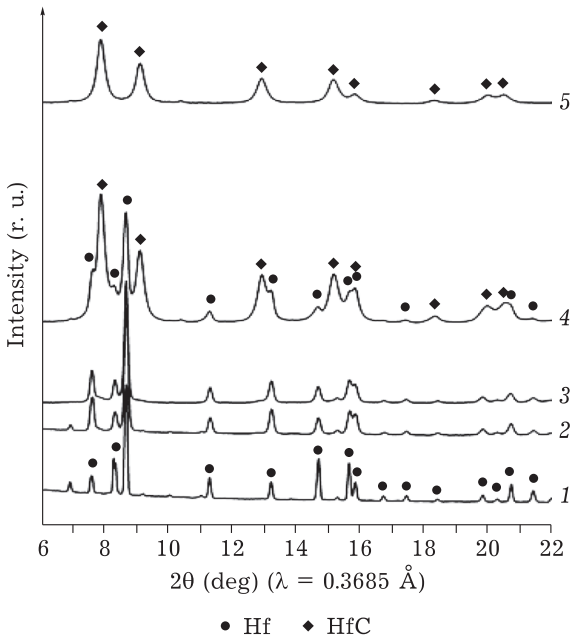

Fig. 2. X-ray diffraction patterns of the initial Hf (*1*) and mixtures of carbon and hafnium after MA for 10 s (*2*), 2 min (*3*), 4 min (*4*), and 8 min (*5*).

patterns (see Fig. 2, curves *2* and *3*). Herewith, their position remains constant.

Increasing activation time to 4 min leads to the formation of a mixture of hafnium (IV) carbide and the Hf/C composite (see Fig. 2, curve *4*). With MA is equal to or higher than 8 min, monophasic ultrafine HfC (see Fig. 2, curve *5*) with 10 nm size of spherical particles is formed (Fig. 3, *a*). According to TEM, particles form aggregates with higher sizes, from ~100 to ~500 nm (see Fig. 3, *b*).

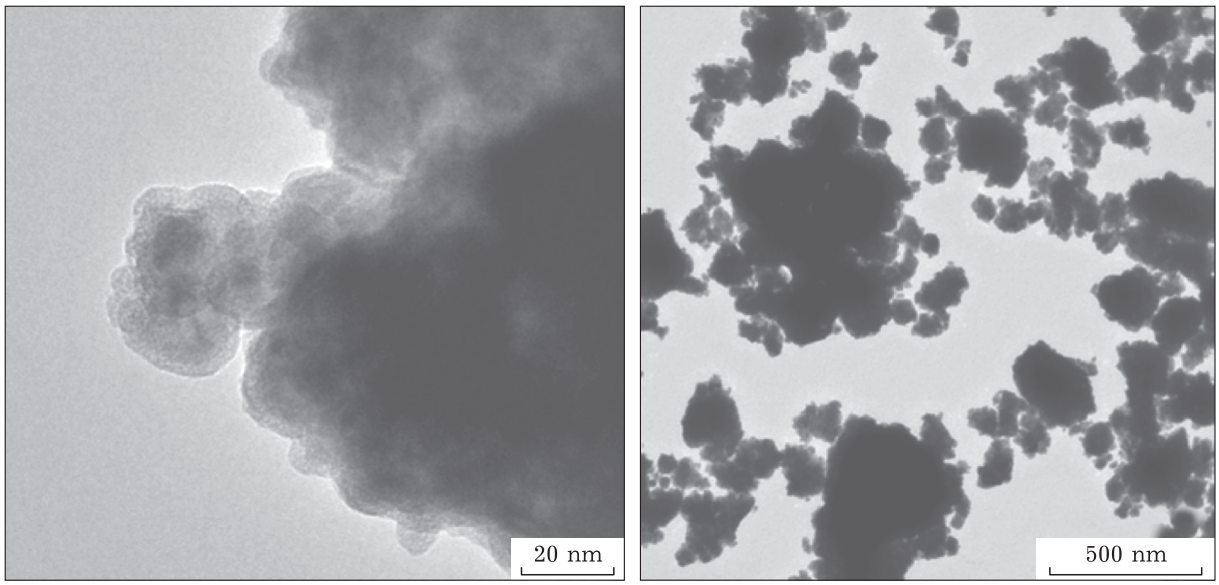

Fig. 3. TEM images of a hafnium (IV) carbide produced during MA for 8 min.

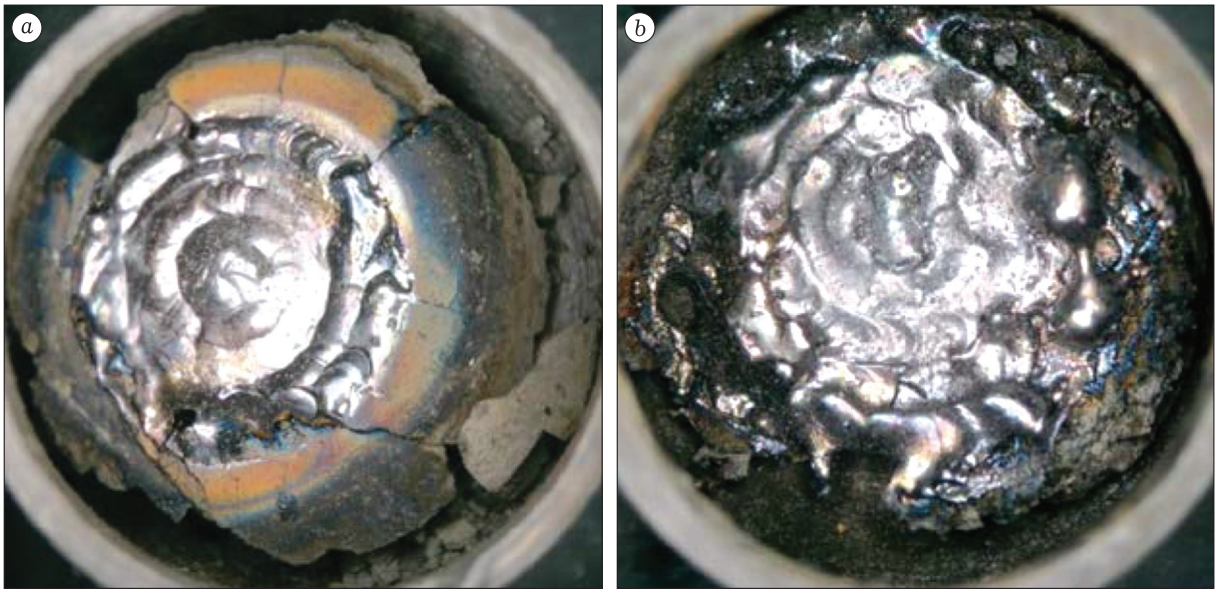

Fig. 4. Fused hafnium (IV) carbide samples produced from the hafnium (IV) carbide powder (*a*) and from the hafnium/carbon mechanocomposite (*b*) under the same conditions.

In order to address the assigned task, the method of treatment of the hafnium/carbon mechanocomposite with highly intense photon flows was used. The technique enables to quickly heat limited sample volume up to high temperatures (above 6000 °C). So high temperatures make it possible not only to initiate the formation process of hafnium (IV) carbide but also to melt it. Protective gas medium is sufficient for laser treatment. This substantially simplifies the process for manufacturing products and allows treatment of large surfaces in great quantities, too.

Two experiments for producing fused hafnium (IV) carbide were carried out. They included the procedure of treatment of the hafnium (IV) carbide powder and the hafnium/carbon mechanocomposite during the exposure of samples to highly intense radiation. As can be seen from Fig. 4, the formation of hafnium (IV) carbide alloy begins earlier than that from hafnium (IV) carbide powder. X-ray diffraction patterns for both samples are identical and coincide with reference ones for HfC.

The thickness of the layer of fused hafnium (IV) carbide present over the layer of the sintered one is 0.3 mm.

CONCLUSION

A set of experiments performed on laser treatment of compressed tablets made of the mechanocomposite hafnium/carbon and HfC powder have revealed the following. It is more efficient to produce fused hafnium (IV) carbide products using the Hf/C mechanocomposite than HfC powder. This is related to the heat release during the reaction of carbon and hafnium. Reflecting power is increased during laser irradiation after HfC melting due to the appearance of free electrons and, accordingly, the risk of sample overheating is reduced.

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