A Co-reduction-carburization Route to Synthesize Nanocrystalline ZrC

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(Received May 13, 2002; CL-020413)

Nanocrystalline zirconium carbide (ZrC) with the size of 10–25 nm was synthesized via a co-reduction-carburization process, in which $ZrCl_4$ and CCl_4 were used as zirconium source and carbon source, respectively, and metallic Na as reductant in an autoclave at 550 °C for 12 h. The samples were characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

Zirconium carbide (ZrC) is a refractory material with a very high melting point and excellent strength, as well as high thermal and electrical conductivities and chemical stability. ZrC particles are used to reinforce the mechanical properties of metal[1] and alloy.[2] In practical applications, ZrC has been used for field-emission device[3] and as catalyst for decomposition of methanol.[4]

In the industrial scale, ZrC is prepared at high temperature using the reaction of Zr, ZrH_2 or ZrO_2 with graphite under vacuum or inert gas and the reaction of Zr or $ZrCl_4$ with carburizing gas (H_2+CO, CH_4 etc).[5] Recently, mechanical alloy method is used to synthesize ZrC powders by ball milling of elemental Zr or ZrO_2 and C powders, then the milled powders are processed at high temperature to obtain crystallites.[6,7] There are also some new routes to synthesis of ZrC: inorganic-organic hybrid firing at 1500 °C in an Ar flow;[8] vapor phase metallizing of micro-coiled carbon fibres and $ZrCl_4$;[9] solid state metathesis routes;[10] Mg-thermite method from ZrO_2-Mg-CH_4 system;[11] pyrolysis of zirconium alkoxide precursors[12] and arc burning of a composite carbon rod containing ZrC.[13]

Based on the previous research work,[14–16] a co-reduction-carburization method, in which $ZrCl_4$ and CCl_4 is used as zirconium source and carbon source respectively and metallic Na as reductant, is utilized to synthesize ZrC nanocrystallites in an autoclave between 500–650 °C. Estimated with the ideal gas law, the pressure in the autoclave under our experiment conditions is about 4 MPa. The reaction can be expressed as follows:

$$ZrCl_4+CCl_4+8Na \rightarrow ZrC+8NaCl \quad (1)$$

All manipulations were carried out in a dry glovebox with N_2 flowing. In a typical procedure, 6.9 g $ZrCl_4$, 3 mL CCl_4 and 5.1 g granular metal Na were put into a stainless steel autoclave of 50 mL capacity. The autoclave was sealed and maintained at 550 °C for 12 h, then allowed to cool to room temperature in the furnace. The product was collected and washed with absolute ethanol, 0.1 M hydrochloric acid and distilled water to remove NaCl and other impurities. After drying in a vacuum at 60 °C for 4 h the black powder was obtained.

The samples were characterized by X-ray powder diffraction (XRD) patterns, which were recorded on a Japan Rigaku Dmax-γA X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The transmission electron microscopy (TEM) images and electron diffraction (ED) patterns were taken with a Hitachi Model H-800 transmission electron microscope. The high-resolution electron microscopy (HREM) images were obtained with JEOL-2010 transmission electron microscope. The Raman spectra were measured by a JY LABRAM-HR Con-focus Laser MicroRaman Spectrometer using an Ar^+ laser excitation with a wavelength of 514.5 nm.

The XRD pattern of sample was shown in Figure 1. All the intensive peaks corresponded to face-center cubic (fcc) ZrC with cell constant $a = 4.686$ Å, which was in agreement with the values in the literature.[17] The average sizes of nanocrystallites estimated from the Debye-Schrrer formula were 18 nm.

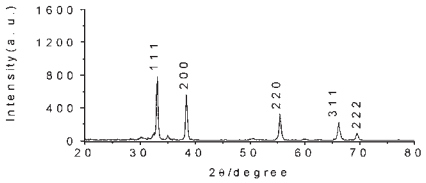

Figure 1. XRD pattern of sample prepared through a co-reduction-carburization reaction using $ZrCl_4$ and CCl_4 as source material and metallic Na as reductant at 550 °C for 12 h.

The morphology of ZrC nanocrystallites was studied by TEM. The photographs of nanocrystalline ZrC were shown in Figure 2a. It can be seen that ZrC crystallites were irregular particles with size ranging from 10 to 25 nm from the TEM micrograph. The selected ED pattern (Figure 2(b)) indicated that the nanoparticles were well-defined single crystal. The regular fringes spacing with 0.238 nm in the HREM image (Figure 2(b)) closed to the distance of 002 lattice planes of fcc-ZrC. It was found that the nanocrystalline ZrC was covered with graphite.

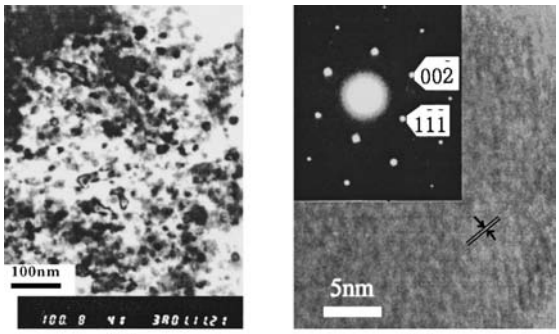

Figure 2. TEM micrograph (a) HREM image (b) of the same ZrC sample as in Figure 1.

This was confirmed by the Raman spectra of the sample (as shown in Figure 3). There were two bands, the D-Band (1350 cm^{-1}) and the G-band (1560 cm^{-1}), in agreement with nanocrystalline graphite.[18]

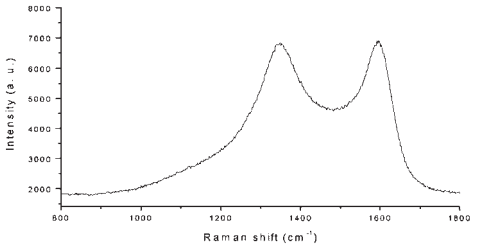

Figure 3. Room temperature Raman spectrum of the same sample as in Figure 1.

The influences of temperature and reaction time on the formation of nanocrystalline ZrC were investigated. At a temperature lower than 380 °C or in a time shorter than 4 h, crystalline ZrC was not formed. When the temperature was higher than 650 °C, the size and crystallinity of ZrC particle increased in the same reaction time. If the ratio of CCl_4 was reduced, the metal zirconium was found in the product judging from the XRD pattern.

ZrC particle may form via a co-reduction-carburization route. According to previous research work[11,14–16] and our experiment results, we thought that the formation of nanocrystalline ZrC might include the following reactions:

$$ZrCl_4+4Na \rightarrow Zr+4NaCl \quad (2)$$

$$CCl_4+4Na \rightarrow C+4NaCl \quad (3)$$

$$Zr+C \rightarrow ZrC \quad (4)$$

Both the reduction reactions of $ZrCl_4$ and CCl_4 with Na were thermodynamically spontaneous and exothermic ((2): $\Delta G_f^\circ = -154.58\,kcal{\cdot}mol^{-1}$, $\Delta H_f^\circ = -158.73\,kcal{\cdot}mol^{-1}$; (3): $\Delta G_f^\circ = -351.68\,kcal{\cdot}mol^{-1}$, $\Delta H_f^\circ = -360.71\,kcal{\cdot}mol^{-1}$).[19] The reaction (4), which formed ZrC product, was also a thermodynamically spontaneous and exothermic reaction ((4): $\Delta G_f^\circ = -47.7\,kcal{\cdot}mol^{-1}$, $\Delta H_f^\circ = -48\,kcal{\cdot}mol^{-1}$).[19] Previous research work[14–16] has illuminated that $ZrCl_4$ and CCl_4 could be reduced by metal Na at a temperature higher than 350 °C. Both the exothermic reduction reaction started at a temperature about 400 °C. According to the work of Kobayashi,[11] the reaction temperature under our experiment conditions raised by the reaction heat might be over 750 °C. Then the particles of ZrC were formed by carburization reaction at high temperature simultaneously. Our carbon source was CCl_4 and reduced with Na, this would be in favor of forming ZrC at low reaction temperatures. This is confirmed by the experimental results: when the CCl_4 was replaced by active carbon, ZrC was not obtained at 600 °C for 12 h by same method.

In summary, a co-reduction-carburization method was applied to synthesize nanocrystalline ZrC. $ZrCl_4$ and CCl_4 were used as zirconium source and carbon source, respectively, and metallic Na as reductant in the route. This will be a method to synthesize other nanocrystalline carbides at low temperatures.

Financial support from the National Natural Science Funds and the 973 Projects of China is gratefully acknowledged.

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