

Chapter 31

Carbon Vacancy Ordered Non-Stoichiometric $\text{ZrC}_{0.6}$: Synthesis, Characterization and Oxidation at Low Temperature

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ABSTRACT

The starting nanopowders of non-stoichiometric zirconium carbide (ZrC_x) were fabricated via milling Zr powders in toluene for different dwell times. The carbon content was determined to depend on the milling time and the used amount of toluene. The bulk non-stoichiometric ZrC_x with different x were prepared by spark plasma sintering of the obtained ZrC_x nanopowders. The microstructural features of a sintered $\text{ZrC}_{0.6}$ sample were investigated via the measurements of XRD, TEM, and HRTEM. It was found that the carbon vacancies have an ordering arrangement in C sublattice, forming a Zr_2C -type cubic superstructural phase with space group of $\text{Fd}\bar{3}m$. Moreover, it was observed that the superstructural phase exists in nano-domains with an average size of ~ 30 nm owing to the ordering length in nanoscale. During the heating treatment in air, it was recognized that the diffusion of oxygen atoms is significantly facilitated through the ordered carbon vacancies. For the heating treatment at low temperature ($< 300^\circ\text{C}$), the oxygen atoms diffuse easily into and occupy the ordered carbon vacancies, forming the oxy-carbide of $\text{ZrC}_{0.6}\text{O}_{0.4}$ with ordered oxygen atoms. At the heating temperature higher than 350°C an amorphous layer of $\text{ZrC}_{0.6}\text{O}_{y>0.4}$ was identified to be formed due to the diffusion of superfluous oxygen atoms into Zr-tetrahedral centers. Inside the amorphous layer, the metastable tetragonal zirconia nanocrystals are recognized to be gradually developed.

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INTRODUCTION

As one of the important refractory materials, zirconium carbide (ZrC) exhibits many excellent properties such as high hardness (Pierson, 1996), good corrosion resistance (Pierson, 1996; Oyama, 1996), good electrical and thermal conductivity (Toth, 1971), the low neutron absorption or scattering cross sections and low damage under irradiation (Ogawa & Ikawa, 1982), etc. Owing to these attractive properties, it demonstrates great potential in the technological applications, such as cutting tools, high-speed aircraft leading edges (Van Wie et al., 2004) operating in high or ultra-high temperature, the thermal-field emitters (Yada, et al., 1989), etc. In past decades, intensive investigations have been carried out on the properties and applications of ZrC . The nonstoichiometric nature of most obtained bulk zirconium carbide has been cognizant (Pierson, 1996), and some ordered phases have also been predicted theoretically (Gusev & Rempel, 1993). However, the experimental studies on the ordered carbon vacancies are pretty rare to date. Furthermore, the studies on the oxidation of nonstoichiometric ZrC_x with $x < 1$ are very insufficient, especially for carbon vacancies ordered phase.

In this chapter, we will introduce the preparation and structural features of carbon vacancy ordered $\text{ZrC}_{0.6}$. The oxidation process and products for this ordered phase are also discussed with the help of XRD, TEM, and HRTEM measurements.

BACKGROUND

ZrC is typical transition metal carbide with the NaCl ground-state crystal structure. In the cubic close packed structure, carbon atoms are filled in the octahedral interstices formed by the Zr atoms. The Zr and C atoms are located at the positions of the 4a (0 0 0) and 4b (1/2 1/2 1/2), respectively. If all the octahedral sites are occupied by C atoms, the stoichiometric monocarbide is formed. In reality,

however, stoichiometry is hard to be reached, and high concentration of carbon vacancies is present at the octahedral sites of the metalloid sublattice (Pierson, 1996). Thus, zirconium carbide is often regarded as a highly nonstoichiometric compound, labeled as ZrC_x ($0.5 < x < 1$). Owing to the high sensitivity of the chemical bonding and electronic structures to the carbon vacancies, the number and arrangement of carbon vacancies have great effect on the properties of ZrC_x , inducing significantly different properties from the stoichiometric ones (Lipatnikov et al., 1997; Zueva et al., 2000; Lipatnikov et al., 1997; Morgan & Lewis, 1974; Valeeva et al., 2009; Miracle & Lipsitt, 1983; Tsurekawa et al., 1983; Obata & Nakazawa, 1976; Gusev & Rempel, 1984). For examples, the enhancement of hardness and yield stress owing to the ordered carbon vacancies have been observed in some transition metal carbides (Miracle & Lipsitt, 1983; Tsurekawa et al., 1983). For carbon vacancies-rich carbides, the carbon vacancies ordered state are considered to be thermodynamically equilibrium at room temperature (Gusev, 2000). However, due to the high melting point of carbides and the low self-diffusion of carbon atoms (Bulychev et al., 1977; Mahday et al., 2000), the carbon vacancies disordered carbides are usually present as metastable phases at room temperature. Large amount of studies have been reported about the ordering in transition metal carbides, such as TiC (Goretzki, 1967; Bell & Lewis, 1971; De Novion & Moisy-Maurice, 1977; Gusev, 1991; 2000; De Novion & Landesman, 1985; Moisy-Maurice et al., 1982), VC (Venables et al., 1968; Billingham et al., 1972; Khaenko et al., 1978; 1979; de Novion et al., 1966) NbC (Gusev & Rempel, 1986; 1994; Rudy & Brukl, 1967; Landesman et al., 1985), etc.. For the nonstoichiometric ZrC_x , Gusev and coworkers (Gusev et al., 2001) predicted theoretically three possible types of ordered phase, i.e. Zr_2C , Zr_3C_2 , Zr_6C_5 , depending on the vacancy concentrations. For each type of ordered phase, there are several types superstructure, depending on the location of the vacancies. Those

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