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Full Length Article

Low-temperature synthesis of nanocrystalline ZrC coatings on flake graphite by molten salts

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ABSTRACT

A novel molten salt synthetic route has been developed to prepare nanocrystalline zirconium carbide (ZrC) coatings on flake graphite at 900 °C, using Zr powder and flake graphite as the source materials in a static argon atmosphere, along with molten salts as the media. The effects of different molten salt media, the sintered temperature, and the heat preservation time on the phase and microstructure of the synthetic materials were investigated. The ZrC coatings formed on the flake graphite were uniform and composed of nanosized particles (30–50 nm). With an increase in the reaction temperature, the ZrC nanosized particles were more denser, and the heat preservation time and thickness of the ZrC coating also increased accordingly. Electron microscopy was used to observe the ZrC coatings on the flake graphite, indicating that a “template mechanism” played an important role during the molten salt synthesis.

1. Introduction

Graphite has attracted significant attention because of its excellent properties such as its high thermal conductivity, thermal shock resistance, and low thermal expansion coefficient [1,2]. Because it has an excellent combination of a layered structure and desirable physical properties, graphite is a promising functional material for a wide range of applications such as in electronic devices, machinery, optics, advanced engineering, and metallurgy industries [1,3–6]. A drawback to the use of graphite is its low water wettability and the poorly homogenized dispersion of graphite materials in castable systems, where the resulting castables flow poorly and considerable water content is required [7,8]. On the other hand, its low oxidation resistance limits its application in a high-temperature oxygen environment. Such a drawback could be overcome by the surface treatment of graphite, which provides wetting and oxidation resistance between the surrounding environment and the graphite surface.

At present, graphite is modified using metals, carbides, or oxides, all of which have better oxidation resistance and water wettability than graphite. To date, many researchers have reported that the oxidation resistance can be improved by coating the surface of graphite [9–18]. Zhang and Lee [19] formed Al_2O_3, Al_2O_3-SiO_2, and SiO_2 coatings on natural flake graphite via the hydration of TEOS($Si(OC_2H_5)_4$) and $Al(OC_3H_7)_3$ in distilled water and reported an improvement in the graphite oxidation resistance and water wettability. Park et al. [20] enhanced the oxidation resistance of graphite and achieved crack healing by applying a thin SiC coating. However, most coating methods require complex, environmentally unfriendly, and expensive manipulations.

In this work, we present a novel way of evenly modifying the surface of graphite using a molten salt synthesis (MSS) method at a relatively low temperature [21–27]. The morphology changes and synthesis mechanism of the ZrC nanocrystals formed on the graphite were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) techniques.

2. Experimental materials and procedure

Zirconium powder (purity ≥ 99% w/w, particle size ≤ 44 μm), graphite (purity ≥ 97% w/w, particle size 200–300 μm), NaF (purity ≥ 99% w/w), LiCl (purity ≥ 99% w/w), NaCl (purity ≥ 99% w/w), and KCl (purity ≥ 99% w/w) were used as the raw materials. The molar ratio of Zr to graphite was 1:3, and mixed salts combined with appropriate amounts of graphite and Zr powder were added. The powder mixture was placed in an alumina crucible and heated at 900–1200 °C in argon using an alumina-tube furnace. After furnace cooling to room temperature, the reacted mass was

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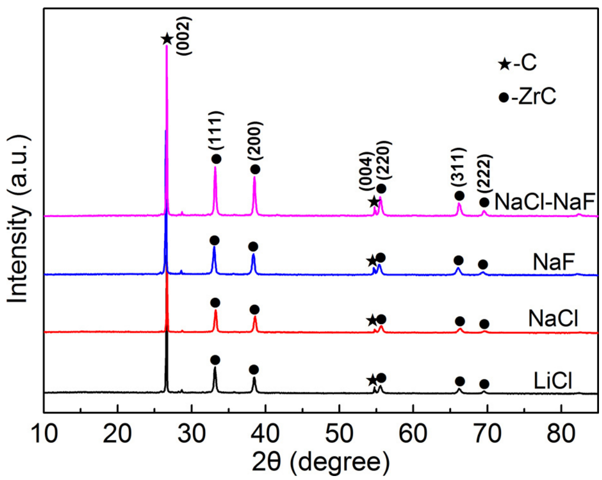

Fig. 1. XRD patterns of samples annealed at 1000 °C for 3 h in different molten salt media.

filtered and washed with deionized water several times to remove the residual salt, until no Cl^- was detected in the filtrate using an $AgNO_3$ solution (i.e., no AgCl precipitation was observed when an $AgNO_3$ solution was added dropwise to the filtrate). The resulting samples were oven-dried overnight at 110 °C before further characterization.

The phases of the resultant powders were studied using XRD (Philips, X'Pert Pro). The ICDD cards used for identification were ZrC (03-065-0332), graphite (01-075-2078), and Zr (01-088-1147). The microstructures and morphologies were observed using SEM (FEI, Nova 400 Nano) and TEM (JEOL, JEM-2000F). In addition, high-resolution TEM was used for lattice-resolved imaging to identify the atomic structure of the ZrC. Selected area electron diffraction (SAED) was used to assist in identifying local phases. The room temperature XPS (AXIS-ULTRA DLD-600W) measurements of the coating were carried out using an Al Kα excitation source, and AFM (SHIMADZU, SPM9700) was employed to examine the coating morphologies.

3. Results and discussion

3.1. Effects of molten salt media and heat preservation time on synthesized nanocrystalline ZrC coatings

In order to study the effect of the molten salt component on the synthesized nanocrystalline ZrC coating, an experiment was conducted to study the effect of different molten salt systems on the in situ synthesized ZrC coated graphite. Zr and graphite were used in different molten salt medium systems. The XRD patterns of samples annealed at 1000 °C for 3 h are shown in Fig. 1. As can be seen in the graph, the diffraction peaks of graphite and ZrC appeared in four kinds of molten salt systems: LiCl, NaCl, NaF, and NaCl-NaF, and the peaks at 2θ values of 33.04, 38.34, 55.34, 65.98, and 69.32 are assigned to the (111), (200), (220), (311) and (222) crystal planes of cubic ZrC with a lattice parameter a = 0.468 nm [28]. This phenomenon can be explained by the ionic strength theory. Ions with a smaller valence number have a faster velocity, which can be adjusted to the uniform grain orientation in the process of combination. The diffraction peak intensity of ZrC was relatively high in the NaCl-NaF molten salt system, which showed that a relatively

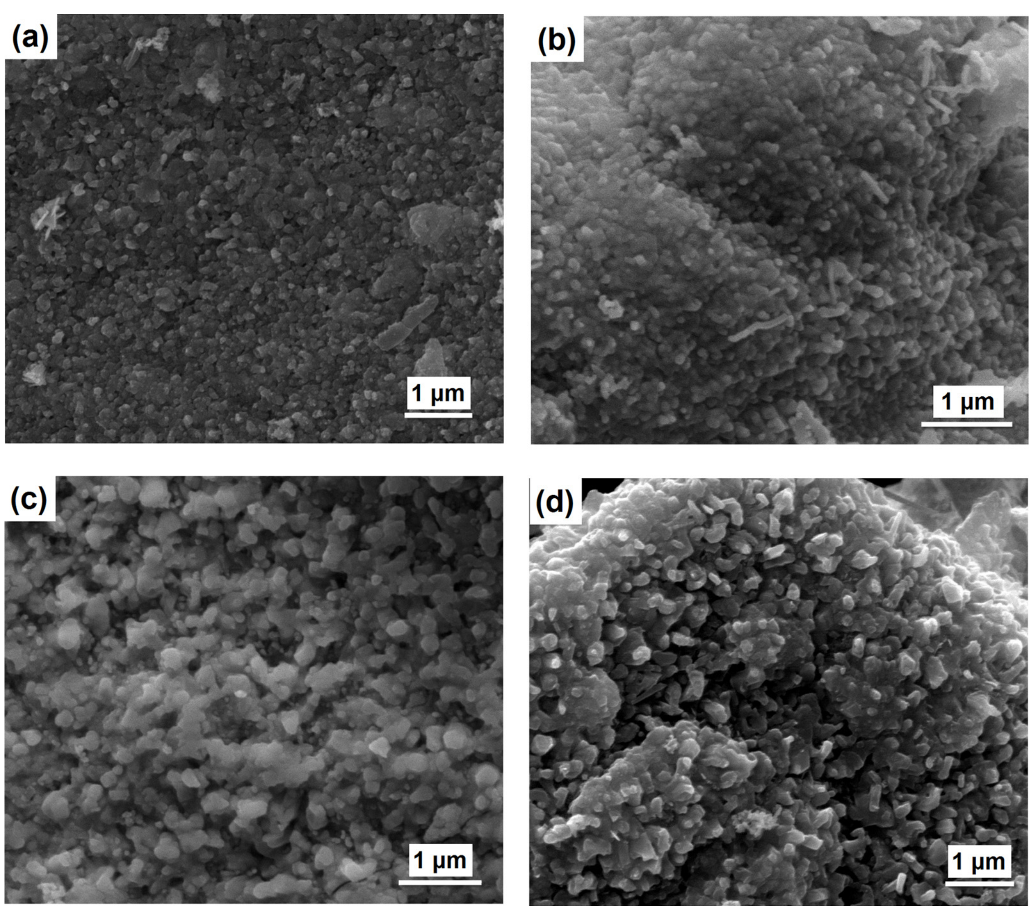

Fig. 2. SEM micrographs of samples sintered at 1000 °C for 3 h in different molten salt media: (a) LiCl, (b) NaCl, (c) NaF, and (d) NaCl-NaF.