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Electrochemical synthesis of NbC−Sn composite powder in molten chloride

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Abstract: NbC−Sn composite powder was successfully prepared from SnO_2, Nb_2O_5 and carbon by electrochemical reduction and carbonization in $CaCl_2$−NaCl molten salt at 900 °C. The reaction pathway was investigated by terminating electrochemical experiments for various durations. The influence of carbon on the final products was considered. NbC particles were obtained by leaching the composite with acid. The results showed that the aggregated NbC−Sn composite powdev contained NbC particles about 50−100 nm and Sn particles about 200 nm. SnO_2 was reduced to Sn in the sintering process. Nb_2O_5 was electrochemically reduced to Nb in molten salt, experiencing some intermediate products of calcium niobates and niobium suboxides. Nb metal obtained was converted to NbC with assistance of carbon. The reduction of Nb oxides may be incomplete and Nb_3Sn would be formed if carbon is insufficient in the cathodic pellet. NbC with good dispersity is produced by leaching NbC−Sn with HCl.

Key words: NbC−Sn; electrochemical reduction; molten chloride; calcium niobates; acid leaching

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1 Introduction

Niobium carbide (NbC) is a non-oxide ceramic material primarily used as the starting material for the commercial production of wear-resistant composites and cutting tools due to its attractive properties of high melting point (3610 °C) [1], good thermal stability, excellent chemical inertness, low friction coefficient, high density [2], extreme hardness and satisfactory mechanical toughness [3−5]. In addition, niobium carbide powder is usually added into other metals or alloys as a reinforcing phase to improve mechanical properties of the metallic matrix [6]. However, there are still some challenges for niobium carbide as the hard phase, such as low wettability and poor sinterability. The insufficient features could be enhanced by adding more ductile materials to form a kind of metal-carbide cemented composite [7−10].

There are some methods to prepare niobium carbide, including carburization of niobium oxide to form niobium carbide [11], mechanical alloying of niobium and carbon [12,13], mechanochemical process of $NbCl_5$ and CaC_2 [14], and self-propagating combustion of niobium and carbon [15]. Most of these methods employ relatively high temperature or hazardous substances, which make them not very environment friendly. Electrochemical reduction in molten salt is an optional route to prepare metal [16,17], metal alloy [18−21], as well as metallic carbides [22−24]. Particularly, it is favorable for preparation of metal-carbide composite by mixing metallic oxide directly into sintered precursor. Some scientists have reported electrochemical synthesis of the cemented powder in molten salt. ZOU et al [25] studied directly electro-preparation of Ti_5Si_3/TiC composite from the oxides/C precursor in molten $CaCl_2$. Our group also reported fabrication of Fe-based TiC and Ni−TaC cemented powder previously, in which Fe or Ni was used as a binder to form metal-carbide composite [10,24]. In general, the operating temperature used in the electrochemical process is energy competitive than that used in other metallurgical methods. It is an advantage

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for generation of dispersive nano-sized carbide particles in metal matrix. But Sn has seldom been reported as metal matrix to support the nano-sized carbide particles in molten salt till now. It should be a little different from Ni, Fe and Si, since the melting point of Sn is obviously lower than the working temperature (231 °C).

In this work, NbC−Sn composite powder was successfully synthesized by electrochemical reduction of Nb_2O_5 in the presence of SnO_2 in molten salt. The possible reaction pathway for electrochemical reduction and carbonization in the melt was investigated. The aim of this work was to prepare NbC−Sn composite powder and dispersived NbC powder in a moderate method.

2 Experimental

All the starting materials were of analytical grade and commercially available. Nb_2O_5, SnO_2 and carbon powder were mixed with a mole ratio of 2:1:3 (Nb/Sn/C) in ethylalcohol, and subsequently ball milled for 1 h. Approximately 1 g of the mixture powder was pressed under a uniaxial pressure of 10 MPa, followed by a sintering process at 1000 °C for 3 h in argon atmosphere. A eutectic mixture of $CaCl_2$ and NaCl with mass ratio of 7:3 was dehydrated at 300 °C for more than 24 h, which was then elevated to the targeted temperature. The schematic illustration of the electrolytic cell is given in Fig. 1. The vessel was sealed and argon gas was flushed into the reactor to clean the air and vapour. Then, the reactor was heated up to 900 °C at a rate of 3 °C/min. Subsequently, pre-electrolysis was carried out between two graphite rods at 2.5 V for 0.5 h to remove possible impurities existing in the melt [26−28]. The sintered pellet was used as the cathode and a high density graphite rod of 13 mm in diameter and 70 mm in length served as the anodes. A constant voltage of 3 V was applied between the electrodes for certain durations immediately after they were immersed into the melt using a WYJ 40A 15V power supply. This voltage provides sufficient electrochemical driving force for deoxidation of niobium oxides, avoiding continuous decomposition of $CaCl_2$ and NaCl. All the experiments were performed under high-purity argon. The sample obtained were removed from the reactor, ultrasonically washed with distilled water and ethylalcohol in sequence, and then dried at 60 °C. Phase composition and morphology were examined by a D/Max−2500PC X-ray diffractometer (XRD) with Cu K_α radiation and a JSM−6360L V scanning electron microscope (SEM) in combination with energy-dispersive X-ray (EDS).

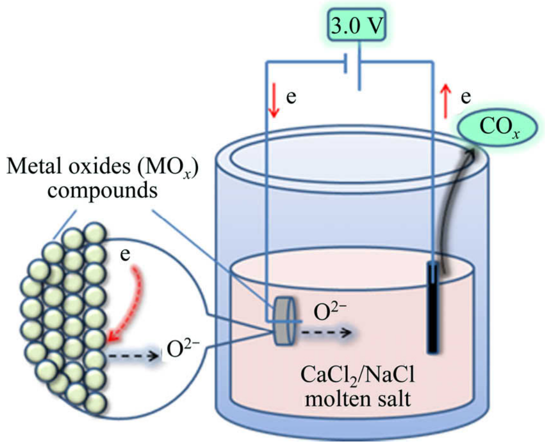

Fig. 1 Schematic illustration of electrolytic cell

3 Results and discussion

3.1 Analysis of sintered pellet

The typical XRD pattern of Nb_2O_5, SnO_2 and carbon powder with a mole ratio of 2:1:3 (Nb/Sn/C) mixture sintered at 1000 °C for 3 h is shown in Fig. 2(a). Characteristic peaks of NbO_2, Nb_2O_5 and Sn can be detected. This indicates that SnO_2 is completely reduced to Sn by carbon in the sintering process, as expressed in Eq. (1). The Sn retrieved from SnO_2 is beneficial for formation of metal-carbide composite in comparison to Sn metal directly mixed into the precursor. It is difficult to crush Sn particles into small pieces because of their good ductility. So, it is not easy to disperse Sn uniformly in the sintered pellet. Furthermore, the loss of Sn is obvious during sintering procedure if Sn metal was added directly into the precursor. The melting point of Sn is 231 °C, while the sintering process was performed at 1000 °C. So, the metal would flow out of the pellet if too much Sn aggregated together in the pellet, as illustrated in Fig. 2(d). Nevertheless, Sn was almost homogeneously mixed without segregation in the pellet if Sn oxide was applied, and the phenomenon of Sn loss is not obvious in Fig. 2(c). Moreover, some Nb_2O_5 was reduced into NbO_2 in the sintering process. In our previous study [4], it was found that Nb_2O_5 maintained to be inert with the presence of carbon at 1000 °C, though reaction between the two chemicals is thermodynamically favorable (Eq. (2)). However, reduction of Nb_2O_5 occurred once SnO_2 was mixed into the precursor. This phenomenon is probably ascribed to CO released from carbothermal reduction of SnO_2 (Eq. (1)), which would participate the reduction of Nb_2O_5 (Eq. (3)). This promotes the transformation from Nb_2O_5 to NbO_2 in the sintered process.

Figure 2(b) shows the SEM image of the composite pellet sintered at 1000 °C for 3 h. The particles of niobium oxide and Sn present different morphologies, and both the sizes are about 1−2 μm. In addition, the carbon additive is about 100 nm in size with an uncrystallized structure, which should be favourable for the formation of carbide [4]. A lot of cavities exist in the pellet, which may result from the evolution of CO gas from carbothermal reduction of SnO_2.