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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<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> and carbon by electrochemical reduction and carbonization in CaCl2-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<sub>2</sub> was reduced to Sn in the sintering process. Nb<sub>2</sub>O<sub>5</sub> 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<sub>3</sub>Sn 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

#### **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<sub>5</sub> and CaC<sub>2</sub> [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<sub>5</sub>Si<sub>3</sub>/TiC composite from the oxides/C precursor in molten CaCl<sub>2</sub>. 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<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub> 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<sub>2</sub> 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



Fig. 1 Schematic illustration of electrolytic cell

deoxidation of niobium oxides, avoiding continuous decomposition of CaCl<sub>2</sub> 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<sub>a</sub> radiation and a JSM–6360L V scanning electron microscope (SEM) in combination with energy-dispersive X-ray (EDS).

#### 3 Results and discussion

#### 3.1 Analysis of sintered pellet

The typical XRD pattern of Nb<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub> 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 NbO2, Nb2O5 and Sn can be detected. This indicates that SnO<sub>2</sub> 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<sub>2</sub>O<sub>5</sub> was reduced into NbO<sub>2</sub> in the sintering process. In our previous study [4], it was found that Nb<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> occurred once SnO<sub>2</sub> 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<sub>2</sub>O<sub>5</sub> to NbO<sub>2</sub> 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  $1-2 \mu m$ . 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<sub>2</sub>.



Fig. 2 XRD pattern (a) and SEM image (b) of Nb<sub>2</sub>O<sub>5</sub>/SnO<sub>2</sub>/C composite pellet sintered at 1000 °C for 3 h, photos of sample with SnO<sub>2</sub> (c) and Sn (d) sintered for 3 h

 $SnO_{2}+2C=Sn+2CO(g)$   $\Delta G^{\Theta}(1000 \ ^{\circ}C)=-130.086 \ \text{kJ/mol}$   $Nb_{2}O_{5}+C=2NbO_{2}+CO(g)$   $\Delta G^{\Theta}(1000 \ ^{\circ}C)=-10.267 \ \text{kJ/mol}$ (2)

$$Nb_{2}O_{5}+CO(g)=2NbO_{2}+CO_{2} (g) \Delta G^{\Theta}(1000 \text{ °C})=41.959 \text{ kJ/mol}$$
(3)

#### 3.2 Phase identification of reduced samples

A series of interrupted experiments were carried out to investigate the reduction pathway. Figure 3 demonstrates the XRD patterns of the reduced samples with electrolyzing durations ranging from 0.5 to 9 h. After 0.5 h of reduction, the phases of NbC, Sn and Ca<sub>3</sub>Nb<sub>2</sub>O<sub>8</sub> were indexed, while the diffraction peaks of NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> disappeared. This implies that niobium oxides including NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> were electrochemically reduced to Nb metal, and carbonization of the reduced Nb subsequently took place. Meanwhile, Nb<sub>2</sub>O<sub>5</sub> without undergoing electro-reduction would combine CaO to generate Ca<sub>3</sub>Nb<sub>2</sub>O<sub>8</sub>. Intercalation of CaO into structure of Nb2O5 makes Ca3Nb2O8 a more stable phase, which would experience a relatively tough reduction process. When the reaction time was prolonged, prevalent niobium ions were continuously reduced. Correspondingly, Ca<sup>2+</sup> and O<sup>2-</sup> ions were released into



Fig. 3 XRD patterns of samples electrochemically reduced from  $Nb_2O_5/SnO_2/carbon$  composite pellets under 3.0 V at 900 °C for various durations

the melt from the structure of  $Ca_3Nb_2O_8$ . This would cause phase evolution to the less intercalation phase of  $Ca_2Nb_2O_7$  in the pellet, which became the most dominant phase after 3 h of reduction. With proceeding of the electro-reduction, the diffraction peaks of calcium niobates decreased gradually, while the intensity of NbC peaks increased reversely. Once the duration reached 6 h, the diffraction peaks of calcium niobates completely disappeared, and the pellet is composed of Sn and NbC. This suggests that electrochemical conversion of niobium oxides to niobium metal was achieved. The trace of reaction among Sn metal, intermediate and final products has not been detected from XRD pattern. The phases in the cathodic pellet remained without variation even if the electrolysis time was long.

According to these results presented above, the possible pathway for electrochemical reduction of Sn-NbC could be predicted. Some Nb<sub>2</sub>O<sub>5</sub> and all NbO<sub>2</sub> were reduced gradually to metallic niobium under the driving force of voltage once the electrolysis started, as presented in Eqs. (4) and (5). Though NbO was not seen in the XRD patterns, it is reasonable to predict its existence as an intermediate product since it is observed usually during direct deoxidation of  $Nb_2O_5$ . Carbothermal reduction of Nb suboxides such as NbO<sub>2</sub> and NbO is possible, but it is obviously less predominant because of the relatively low working temperature, in comparison with electrochemical reduction from our previous study on electro-synthesis of niobium carbide in molten salt. Carbon powder would react with the reduced Nb to generate NbC (Eq. (6)). Meantime, Nb<sub>2</sub>O<sub>5</sub> without experience of electro-deoxidation combined CaO in the melt to form a series of calcium niobates (Eq. (7)), which are more difficult to recover in contrast to  $Nb_2O_5$ . Calcium niobates were decomposed gradually to niobium with the proceeding of electrolysis, and NbC was obtained as the final product (Eq. (8)). Sn metal in the pellet maintained to be inert without phase transformation throughout the electrochemical process. On the anode, the ionized O<sup>2-</sup> was oxidized to evolve CO/CO<sub>2</sub> gas with participation of carbon.

NbO+C=Nb+CO(g) (4)

 $Nb_2O_5 + 2e = 2NbO_2 + O^{2-}$  (5)

$$Nb+C=NbC$$
 (6)

 $Nb_2O_5 + xCaO = Nb_2O_5 \cdot xCaO, x = 2, 3$ (7)

$$Nb_2O_5 \cdot xCaO + 2C + 10e = 2NbC + 5O^{2-} + xCaO, x = 2, 3$$
 (8)

The morphologies of products reduced for different reaction time are illustrated in Fig. 4, and EDS analyses for the regions marked in the images are shown in Table 1. Some particles present in Fig. 4(a) have angular shape, whose size is about 3  $\mu$ m on average. The particles should be mainly composed of Ca<sub>3</sub>Nb<sub>2</sub>O<sub>8</sub> since the Ca to Nb mole ratio in region '1' is about 1.37 : 1. This means that CaO began to penetrate into Nb<sub>2</sub>O<sub>5</sub> to form calcium niobates.

After 3 h of reduction, calcium niobates became the most predominant phase in the cathodic pellet, as displayed in Figs. 4(b)-(d). Particles more than 50 µm were observed across the sectional region of the whole

pellet, especially on the surface area of the cathode. This indicates that intercalation of CaO into the cathode is the most notable process, which makes the particles grow up to be big ones [29]. The concentration of CaO is relatively high on surface area of the pellet, where the formation of calcium niobates is remarkable. This observation is in agreement with phase determination in the XRD pattern.

When the pellet was electrolyzed for 4.5 h, the large niobates particles were broken up to relatively small particles with angular shape, as can be seen in Fig. 4(e). The mole ratio of Ca to Nb is about 1.1:1, and O content has been decreased from 56.3% to 11.7% (mole fraction). This implies that calcium niobate was further electrochemically decomposed. When the reduction time was longer than 6 h, the cathodic pellet basically contained NbC-Sn particles. Calcium niobates were almost consumed up except some tough particles, which also decreased with reaction duration, as shown in Figs. 4(e)-(g). In point 3, the Ca to Nb mole ratio is 0.29:1. This means that calcium ions enter into the molten salt with the reduction of calcium niobate. For comparison, it took about 13.5 h from Nb<sub>2</sub>O<sub>5</sub> to the final product of NbC during direct preparation of niobium carbide. The efficiency enhancement for reduction may be attributed to the existence of Sn in the pellet. Our experiment introduced an excellent conductive phase to accelerate electro-deoxidation of the pentavalent niobium compounds.

# 3.3 Influence of carbon amount and preparation of dispersive NbC

The influence of carbon content on the final products was further investigated by varying the mole ratio of Nb, C and Sn in the precursor. Figure 5 gives XRD patterns of the pellets with various compositions electro-chemically reduced at 3.0 V for 12 h. Phase composition of the electrolytic products varied with initial mole ratio of the elements. If carbon is insufficient in the pellet (the mole ratio of the Nb/Sn/C is 2:1:1), some NbO was found besides NbC in the electrolytic product. This signifies that carbon takes a positive role on reduction of niobium oxide. Additionally, Nb tended to combine Sn to form Nb<sub>3</sub>Sn without carbon, and Sn phase can hardly be observed. But phases in the products changed little if excessive carbon (Nb/Sn/C of 2:1:2 to 2:1:4) was added into the precursor. Carbon excluded in carbonization would exist in the product, which was not documented in XRD patterns because of its uncrystallized structure.

Figure 6(a) demonstrates the SEM image of the cathode pellet with the Nb/Sn/C mole ratio of 2:1:3 after electrochemical reduction at 3.0 V for 12 h. Obviously, the typical Nb<sub>2</sub>O<sub>5</sub>·xCaO particles disappeared. The



**Fig. 4** SEM images of samples electrochemically reduced for 0.5 h (a), 3 h (b), enlarged images (c, d) of areas A and B in (b), 4.5 h (e), 6 h (f), 9 h (g) under 3.0 V at 900 °C

Table 1	EDS	analyses	of points	1, 2, 3	marked	in Fig. 4
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Point –	Mole fraction/%						
	С	0	Ca	Nb	Sn		
1	15.27	56.29	15.58	11.34	1.52		
2	43.11	11.71	23.26	20.51	1.24		
3	30.82	47.83	4.55	15.45	0.78		

cathodic pellet is comprised of spherical Nb particles and Sn particles with angular shape. NbC and Sn particles aggregate closely with respective size 50–100 nm and 200 nm. Subsequently, the NbC–Sn composite was leached by 18% HCl aqueous solution at 25 °C for 20 h to remove Sn metal. Figure 6(b) shows the XRD pattern for the leached product. It can be seen that Sn was eliminated in the leaching treatment, while NbC maintained inertness. In contrast to the aggregated morphology of Sn–NbC, carbide obtained is much more dispersive and porous, as illustrated in Fig. 6(c). The production is ascribed to the existence of Sn metal in electro-reduction of niobium oxide, since it can hinder interconnection of NbC particles to generate aggregated ones.



Fig. 5 XRD patterns of samples electrochemically reduced from  $Nb_2O_5/SnO_2/carbon$  composite pellets with different mole ratios of Nb/Sn/C under 3.0 V for 12 h at 900 °C



Fig. 6 SEM image of sample (Nb/Sn/C mole ratio=2:1:3) electrochemically reduced under 3.0 V for 12 h at 900 °C (a), XRD pattern (b) and SEM image of sample leached by 18% HCl (c)

#### 4 Conclusions

1) NbC–Sn composite powder is successfully synthesized by carbothermal reduction of  $SnO_2$ , electrochemical reduction of  $Nb_2O_5$  and carbonization in  $CaCl_2$ –NaCl molten salt. The product is composed of aggregated particles, including NbC particles about 50–100 nm and Sn particles about 200 nm. Dispersive NbC particles about 50 nm in size are obtained by treatment of the product with HCl.

2) Niobium oxides are electrochemically reduced gradually to metallic niobium, and subsequently converted to NbC with the assistance of carbon. Meanwhile,  $Nb_2O_5$  without electro-deoxidation combines CaO in the melt to form a series of calcium niobates. Consequently, niobates are electrically converted to Nb and final product of NbC.

3)  $\text{SnO}_2$  is thermally reduced to Sn metal by carbon in the sintering process. It is favorable for dispersive residence of Sn metal in the precursor and formation of NbC–Sn composite. Sn metal in the pellet is inert throughout the electrochemical process. The presence of Sn enhances the efficiency of electrochemical reduction of niobium oxides.

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摘 要:研究在 900 ℃ 的 CaCl<sub>2</sub>-NaCl 熔融盐体系中,以 SnO<sub>2</sub>、Nb<sub>2</sub>O<sub>5</sub> 和碳粉为前驱体,使用电化学还原和原 位碳化的方法,成功制备出 NbC-Sn 复合粉体材料。通过对不同反应阶段的产物进行分析,研究反应过程机理。 考察前驱体中碳粉物质的量变化对最终产物的影响,并通过酸浸 NbC-Sn 粉体的方式制备 NbC。研究表明通过该 方法制备出尺寸分别为 50~100 nm 和 200 nm 的 NbC 和 Sn 颗粒,两者紧密地聚集在一起。SnO<sub>2</sub> 在烧结过程中被 碳还原为金属 Sn,Nb<sub>2</sub>O<sub>5</sub> 在熔盐中被逐步电化学还原为金属 Nb,并与碳反应生成 NbC。其中,历经了铌酸盐的 形成与分解、低价铌氧化物的形成与进一步还原等过程。当阴极片中的碳不足时,会造成铌氧化物还原不完全并 形成 Nb<sub>3</sub>Sn。复合粉体材料通过 HCl 水溶液浸出,能够获得分散性很好的 NbC 粉体材料。 关键词: NbC-Sn;电化学还原;氯化物熔盐;铌酸钙;酸浸

(Edited by Xiang-qun LI)