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Electrochemical synthesis of Nb_5Si_3 intermetallic compound from molten calcium chloride salt

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ABSTRACT

Nb_5Si_3 intermetallic compound was directly synthesized via an electrodeoxidation process from molten $CaCl_2$ electrolyte. The reaction mechanism was studied by performing a series of quenching investigations, which suggested that the formation of a series of sub oxides and compounds containing calcium and oxygen preceded the formation of Nb_5Si_3. While Nb_2O_5 was gradually reduced to its sub oxides, (Nb_2O_5/NbO_2/NbO/Nb), SiO_2, on the other hand, got directly reduced to silicon and reacted with Nb to form Nb_5Si_3.

1. Introduction

Nb–Si based ultrahigh temperature alloys possess higher melting points, relatively lower densities and attractive high temperature strength comparable with Ni or Al based superalloys [1]. In the Nb–Si based alloys, Nb_5Si_3 is labeled as one of the most promising new generation high temperature materials, because of its excellent performance in high-temperature resistance furnace, low density (7.16 g/cm^3) and outstanding specific mechanical properties at elevated temperatures [2]. Generally, this alloy is prepared through a melting technique in an arc melting furnace. Multiple re-melts are required to get a homogeneous alloy phase. Besides, the loss of silicon through volatilization is inevitable in the high-temperature reaction condition. Alloys have also been synthesized by powder metallurgy (PM) techniques, such as self-propagating high-temperature synthesis (SHS) [3–5], hot isostatic pressing (HIP) [6], element powder metallurgy (EPM) [7], and pre-alloy powder metallurgy [8]. However, these processes offer very little scope for commercial exploitation on account of overall high manufacturing cost.

Recently, a novel electrodeoxidation technique has been developed for fabricating high temperature metals and their alloys. This technique involves removal of the oxygen from oxides(s), when the latter is cathodically polarized in a pool of molten calcium chloride based electrolyte and, thereby, help transform the oxide to its constituent metal(s)/alloy(s) [9]. A series of metals and alloys have been directly produced from their oxides via electrodeoxidation in molten $CaCl_2$ [10–18]. The main advantages of the electrodeoxidation process compared with other extractive metallurgical processes include: its simplicity; low energy and labor requirements; and ability to directly reduce a combination of different metal-oxides to form alloys. In light of the successful applications of electrodeoxidation process, this study under taken to directly produce Nb_5Si_3 intermetallic compound via electrodeoxidation in molten $CaCl_2$.

2. Experimental

In order to prepare the pellet, commercially available Nb_2O_5($\geq$99.99%, particle size: 100 μm) and SiO_2($\geq$99.5%, particle size: 50 ± 5 nm) powders were precisely weighted out in a molar ratio of Nb_2O_5: $SiO_2 = 5:6$ and well mixed with a mortar and pestle. The mixed powder was uniaxially pressed into a pre-formed pellet (0.01 m in diameter and 0.005 m in height), which was then sintered in a muffle furnace at 1100 °C for 4 h. The operation ensured that the pellets had an adequate mechanical strength during subsequent electrodeoxidation step [17–19]. A well prepared electrolyte is essential to gain a desired product. 200 g $CaCl_2$($\geq$96.0%) was weighed out and placed in a well sealed vacuum drying oven (200 °C and 0.02–0.09 MPa) for 24 h. Then, the

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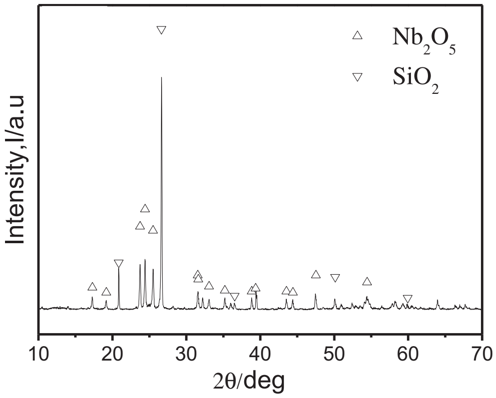

Fig. 1. Powder XRD pattern of the pre-formed pellet sintered at 1100 °C for 4 h.

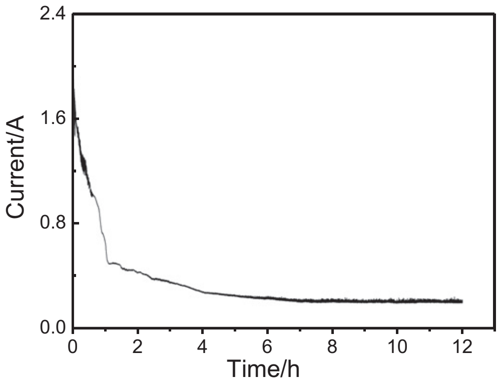

Fig. 3. A typical current-time curve for the electrodeoxidation of a prepared oxides pellet (10 mm in diameter and 5 mm in height) under a constant voltage of 3.0 for 12 h.

preliminary deposited salt was melt in a vertical tubular furnace (900 °C) which was protected by argon air and the pre-melted $CaCl_2$ was conserved in a dry system.

The electrodeoxidation experiment was conducted in a gas tight system at about 900 °C. A recrystallized alumina crucible (0.076 m outer diameter, 0.07 m inner diameter, 0.12 m height, and 0.003 m thickness) that contained pre-melted $CaCl_2$ was kept in a cylindrical alumina (0.08 m inner diameter, 1 m height tube) that was placed in a vertical tubular furnace. The reactor was made gastight with the help of suitable metallic clamps and rubber O ring. A stainless steel rod, wired to the oxide pellet, and a graphite rod (0.006 m in diameter) were used as cathode and anode, respectively. The cathodic product was obtained by electrolyzing the sintered pellet at 900 °C in molten calcium chloride under a constant voltage of 3 V.

The analytical measurements involved phase and microstructure analyses of the reduced samples. The phase composition of the samples was determined by powder X-ray diffraction analysis (Model MAC, M21XVHF22). The microstructural compositions were analyzed by a scanning electron microscope coupled with energy dispersive X-ray analysis (JEOL, JSM-6701F).

3. Results and discussion

Fig. 1 indicated that no new phase other than Nb_2O_5 and SiO_2 was formed during the sintering stage. SEM photographs, Fig. 2(a–d), suggested a compositional homogeneity, with respect to the distribution of niobium, oxygen and silicon, throughout entire cross section of the sintered pellet, which is a prerequisite for obtaining a better Nb_5Si_4 alloy.

Fig. 3 showed the current *vs*. time profile of an electroreduction reaction at an applied voltage of 3 V. Fig. 3 clearly displayed three distinct features, an initial sharp rise(up to ∼2.0 A) followed by

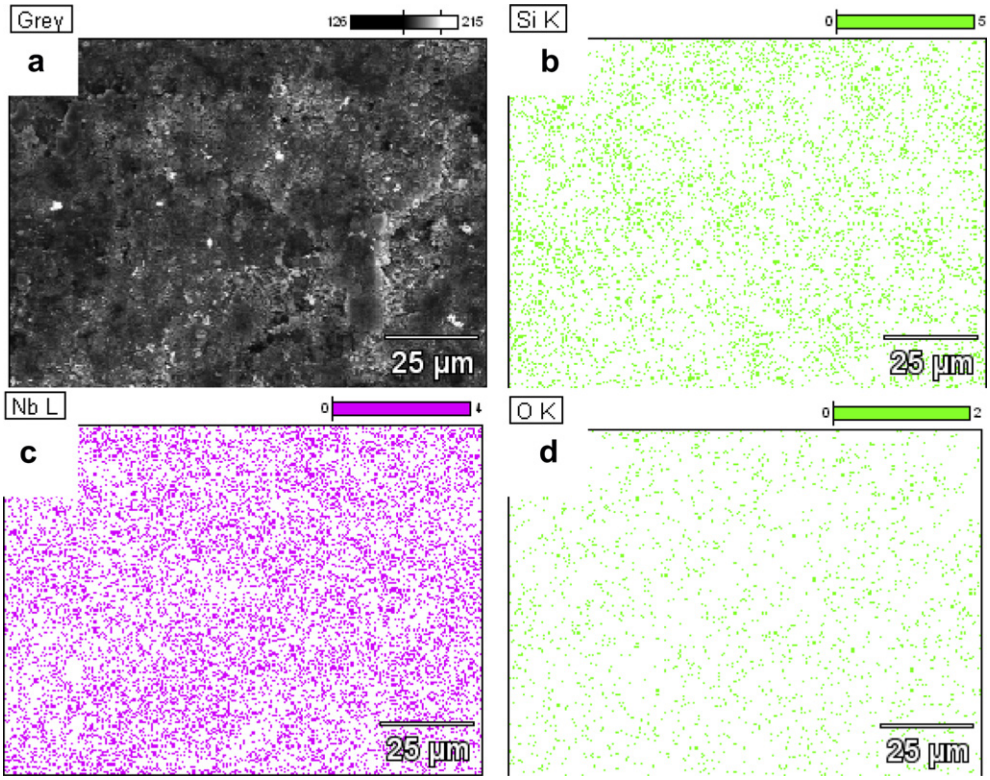

Fig. 2. The SEM image (a) and elements maps (b–d) of the pre-formed pellet sintered at 1100 °C for 4 h.