In-situ Electrochemical Synthesis of Core-shell Structural NbC@Nb5Si3/Nb Composites in Molten Salt

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Abstract. Core-shell structural NbC@Nb5Si3/Nb composites were synthesized from Nb2O5, SiO2 and carbon in molten CaCl2-NaCl salt by electrochemical reduction. Carbon combined with the reduced metal niobium to form NbC core with a diameter of 40nm, and Nb5Si3/Nb as the metal shell. A strong bonding between NbC and Nb5Si3/Nb is benefit for the in-situ compound. The addition of NbC phase could improve the room temperature fracture resistance and reserve the high temperature strength of Nb5Si3/Nb. In order to better understand the reaction mechanism of the electro-deoxidation process, partially reduced samples were obtained by interrupting the reduction process after different reaction times, and examined by XRD, SEM with EDS and TEM analyses.

Keywords: Core-shell structure, NbC@Nb5Si3/Nb, molten salt, in-situ electrochemical synthesis.

1. Introduction
Aerospace presents an extremely challenging environment for structural materials and the development of new, or improved, materials: processes for material and for component production are the subject of continuous research activity [1-3]. The raising of turbine inlet temperature of advanced aero-engine has put forward new requirements for the heat tolerance capacity of components [4]. However, traditional high-temperature alloys based on iron, cobalt and nickel have been difficult to meet the ever-growing demands [5]. The maximum application temperature of single crystal nickel-base materials is 1100℃, approaching the melting point of nickel-based alloys (1350℃) [6-8]. Hence, how to further improve the high-temperature endurance of nickel-based alloys is extremely urgent.

Recently, refractory metals and their intermetallic compounds are one of the promising alternatives to nickel-based superalloys on high-temperature environment [9, 10]. Thanks to the high melting point (2515℃), high hardness, low density (7.16g/cm3) and high temperature strength [11], in-situ Nb/Nb2Si3 composites have been considered as potential materials applied in this field, for instance, the hot rotating parts of aerospace gas turbine engines.
It is well-known that eutectic and eutectoid reactions can take place in Nb–Si binary phase alloys, which provides reliable methods to control their microstructure to improve room temperature fracture toughness of the brittle silicide [12-17]. In addition, high temperature strength will be achieved by the equilibrium between silicide and Nbss up to high temperature. However, incorporation of ductile Nbss phase normally decreases the high-temperature strength of the in-situ composites, since Nbss phase is remarkably weakened at elevated temperature. Therefore, one of the major issues in developing Nb-Si based intermetallic alloys as high-temperature structural materials is to improve room-temperature fracture resistance without sacrificing high-temperature strength. One possible way to meet such requirements is ternary alloying.

In recent years, a large number of studies have been carried out on Nb-Si phase transition process, phase composition, toughness at room temperature and oxidation resistance at high temperature with various alloying elements including Cr, Ti, Hf, W, Mo, Al, B, Zr, Ta, Sn and Y [18, 19]. Kim et al. found that the addition of NbC could improve the structural toughness of Nb5Si3/Nb composites at room temperature [20]. At present, only a few studies focus on the application of carbon in Nb-Si composites to increase their toughness at room temperature, and even fewer studies concern about the mechanism of NbC phase to improve the toughness of niobium silicon composites.

Herein, core-shell structural NbC@Nb5Si3/Nb composites were fabricated from Nb2O5, SiO2 and carbon in molten CaCl2-NaCl salt by electrochemical reduction. Hence, in the experiments carbon is chosen as alloying elements to form a highly stable carbides in the Nb5Si3/Nb composites. Nb2O5 and SiO2 were reduced to Nb and Si, then Nb reacts with Si and carbon to form Nb5Si3 and NbC, respectively. The in-situ method ensures a tight bind between NbC core and Nb5Si3/Nb metal shell, and also can avoid contamination of impurities in the reaction. In addition, reaction mechanism of the electro-deoxidation process was further investigated.

2. Experimental

All the starting materials were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The powder of Nb2O5, SiO2 and carbon powder were mixed with a specific molar ratio of Nb/Si/C in ethanol and ball milled for 1h. Then 1.0g mixture was pressed into a cylindrical pellet with 15mm in diameter and 1.5mm in thickness under a uniaxial pressure of 10MPa, followed by a sintering process in an argon atmosphere at 1000°C for 3h to gain the mechanical strength for the further experiments. The sintered pellet was attached to a stainless steel wire as the cathode, a high-density graphite rod with 13mm in diameter and 70mm in length was employed as the anode. A mixture salt of CaCl2 and NaCl with mass ratio of 7:3 was heated at 300°C for more than 24h to remove the water, then it was transferred into the reactor and heated to 3°C min⁻¹ at 900°C. Pre-electrolytic was carried out between two graphite rods at 2.5V for 2h for removing the impurities and crystal water existing in the melt [21, 22].

The electrochemical reduction was conducted at a constant voltage with a WXY40A 15V power supply in the atmosphere of high purity argon. This voltage provides sufficient electrochemical driving force for oxides reduction reaction. All the experiments were performed under high-purity argon. The samples obtained were washed with distilled water and ethyl alcohol several times, and then dried at 60°C [21, 22]. Phase composition and morphology were determined by D/Max-2500PC X-ray diffractometer (XRD) with Cu K radiation, and the morphology and structure were characterized via a JSM-6360L V scanning electron microscope (SEM) equipped with energy-dispersive X-ray (EDS) and a JEM-2010 transmission electron microscope (TEM).
3. Results and Discussion

3.1. Preparation of Nb$_5$Si$_3$/Nb/NbC composites

3.1.1. Preparation of Nb$_2$O$_5$, SiO$_2$ and carbon cylindrical pellet.

![Figure 1](image1.png)

Figure 1. (a) SEM image of cylindrical pellet pressed from Nb$_2$O$_5$, SiO$_2$ and carbon powders with a Nb/Si/C molar ratio of 6:3:1. (b and c) EDS spectra obtained from Point 1 and 2, respectively.

Fig.1a demonstrates the SEM image of cylindrical pellet pressed from Nb$_2$O$_5$, SiO$_2$ and carbon powders with a Nb/Si/C molar ratio of 6:3:1 after ball-milled with 600 rotate speed for 30 minutes. From Fig.1b and 1c, we can conclude that the obvious angular structural particle with 5μm in diameter in Point 1 is SiO$_2$. The other particles with 1.5μm in size, Point 2 for instance, can be regarded as Nb$_2$O$_5$ (Fig.1c). Carbon powder with nanosize was filled into the gaps of large particles, as a result, it cannot be obviously observed. After the high energy ball milling, no reaction occurs, suggesting that ball milling treatment shows scarcely any influence on the composite of raw materials.

3.1.2. The influence of electrolytic temperature. Fig.2 shows the XRD patterns of electrochemical reduced samples from the molten salt at 700℃ and 900℃. The intensities of diffraction peaks for NbC and Nb$_5$Si$_3$ at 900℃ are both higher than that at 700℃, indicating that a higher electrolytic temperature is favorable for NbC and Nb$_5$Si$_3$ formation. This may result from the lower viscosity of the molten salt at higher temperature, which would facilitate ion transport and further accelerate the reduction.

![Figure 2](image2.png)

Figure 2. XRD patterns of Nb/Si/C with a mole ratio of 6:3:1 electrochemically reduced under 3.0V for 12h at 700℃ and 900℃.
3.1.3. The influence of electrolytic time. In order to investigate the pathway of reduction and subsequent carbonization, the experiment was terminated to obtain the incompletely reduced samples. Fig.3 shows the XRD patterns of the samples reduced for different durations. After 1h of electrolytic reduction, Nb metal became the predominant phase apart from NbC and Ca$_4$Nb$_2$O$_9$ (Eq. (1)-Eq. (3)). No peaks of niobium oxides can be observed, indicating that it has completely consumed: partial Nb$_2$O$_5$ combined with CaO to form calcium niobates (Eq. (1)), the other was reduced to Nb (Eq. (3)). In addition, no Si or Nb$_5$Si$_3$ can be detected after 1 h electrolytic reduction, demonstrating that Nb$_2$O$_5$ has better reduction property than SiO$_2$. The peak strength of Ca$_4$Nb$_2$O$_9$ gradually weakens and almost disappears at 4.5h, indicating that Ca$_4$Nb$_2$O$_9$ begins to decompose (Eq. (4)). SiO$_2$ and Nb show similar condition to that of Ca$_4$Nb$_2$O$_9$, correspondingly, the diffraction peak of Nb$_5$Si$_3$ gradually appears, indicating that SiO$_2$ was reduced to Si, and then further combines with Nb to form Nb$_5$Si$_3$ (Eq. (5)-Eq. (6)). Meanwhile, Nb also reacts with carbon, consequently, the fraction peaks of NbC are increasing with prolonged time. As a result, the final product in the pellet would be Nb$_5$Si$_3$/NbC.

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\begin{align*}
\text{Nb}_2\text{O}_5 + 4\text{CaO} & \rightarrow \text{Ca}_4\text{Nb}_2\text{O}_9 \quad (1) \\
\text{Nb}_2\text{O}_5 + 10e^- & \rightarrow 2\text{Nb} + 5\text{O}^{2-} \quad (2) \\
\text{Nb} + \text{C} & \rightarrow \text{NbC} \quad (3) \\
\text{Ca}_4\text{Nb}_2\text{O}_9 + 10e^- + 2\text{C} & \rightarrow 4\text{Ca}^{2+} + 9\text{O}^{2-} + 2\text{NbC} \quad (4) \\
\text{SiO}_2 + 4e^- & \rightarrow \text{Si} + 2\text{O}^{2-} \quad (5) \\
5\text{Nb} + 3\text{Si} & \rightarrow \text{Nb}_5\text{Si}_3 \quad (6)
\end{align*}
\]

Figure 3. XRD patterns of Nb/Si/C with the mole ratio of 6:3:1 electrochemically reduced under 3.0V for different duration at 900°C.

3.2. Phase and morphology analysis of NbC-Nb$_5$Si$_3$

Fig.4 shows the XRD pattern, SEM image and EDS analysis of sample Nb/Si/C with the molar ratio of 6:3:1 heated in 900°C for 12h. From the XRD pattern, it can be seen that the final electrolysis product is consisted by NbC, α-Nb$_5$Si$_3$ and γ-Nb$_5$Si$_3$. Fig.4b shows that Nb$_5$Si$_3$-NbC particles with integrated sphere structure present a homogeneous particle size around 100nm.
Figure 4. (a) XRD pattern and (b) SEM image of Nb/Fe/C with the mole ratio of 6:3:1 electrochemically reduced for 12h.

In order to further investigate the microstructure of NbC@Nb5Si3/Nb composite, TEM analysis was performed as shown in Fig.5. The NbC@Nb5Si3/Nb composite material shows core-shell structure. Four or five NbC particles with 40nm in diameter are uniformly wrapped in a ductile shell of Nb5Si3 and Nb metal compound with a thickness of 10nm. The core-shell structural composite with NbC as the core, Nb5Si3 and Nb as the shell has better hardness and strength than that of Nb5Si3. This allows Nb5Si3 to be used more widely.

Figure 5. TEM image of the (a) Nb5Si3-NbC sample; (b) the enlarged image of (a).

4. Conclusions
In this work, core-shell structural NbC@Nb5Si3/Nb composites were fabricated via electrochemical reduction in molten CaCl2-NaCl at 900℃. The in-situ synthesis method makes the shell Nb5Si3/Nb metal bond tight with the core NbC. This core-shell structure could improve the property of Nb–Si base intermetallic alloys at high temperature. In order to better understand the reaction mechanism of the electro-deoxidation process, partially reduced samples were obtained by interrupting the reduction process at different reaction temperature and time. This work would shed new light on aerospace high temperature materials.

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