



Preparation of Nb₃Al powder by chemical reaction in molten salts

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Abstract Nb₃Al nanoparticles were directly synthesized by metallothermic reduction process in the molten salts with $m\text{NbCl}_5-n\text{AlCl}_3$ powders as raw materials and sodium as reducing reagent. The effects of different feeding material orders, soaking time, Nb content in raw materials, and $3\text{NbCl}_5-\text{AlCl}_3$ content in molten salts on the obtained Nb₃Al powder were discussed. The as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). It is found that the only phase Nb₃Al nanoparticles are obtained by controlling the variation of the feeding material orders, soaking time, and Nb content in raw materials. And the morphologies of as-prepared nanoparticles change owing to different $3\text{NbCl}_5-\text{AlCl}_3$ contents in molten salts.

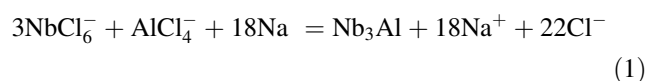
Keywords Chemical reaction; Nb₃Al nanoparticles; Feeding material orders; Molten salt

1 Introduction

Nb₃Al intermetallics received considerable attention as ultra-high-temperature structural materials and superconducting

materials, due to its high melting points, relatively low density, high strength, excellent oxidation and creep resistance, and excellent superconductivity [1, 2]. In particular, Nb₃Al is recognized as excellent source for future superconducting multifilamentary conductors at magnetic fields of much higher than 25 T, under extreme mechanical and irradiation conditions, because of low upper critical field (H_{C2}) values of 21 T at 4.2 K, low critical temperatures (T_c), and high critical current density (J_c) in low fields of <14 T [3, 4]. Therefore, Nb₃Al intermetallics are possibly applied for turbine blades in aircraft engines and stationary gas turbines, perhaps for nuclear magnetic resonance and nuclear magnetic imaging magnets [5–9]. However, it has the lack of deformability and brittle, which leads to fracture and low ductility at room temperature and makes it machine difficulty [10]. In the previous studies, the powder-metallurgical method is considered as an effective way to solve this problem [11], so the preparation of Nb₃Al powders is very important.

Recently, in our previous work, a new direct synthesized process for Nb₃Al intermetallic nanoparticles was developed. In this process, a pure Nb₃Al nanoparticle was directly synthesized from the mixture niobium oxide and aluminum oxide or niobium chloride and aluminum chloride raw material powders by chemical reaction process in the molten salts [12–16]. In this work, the purpose is to control the purity and morphology of the directly synthesized Nb₃Al nanoparticles by changing experimental conditions, such as feeding material orders, soaking time, Nb content in raw materials, and $3\text{NbCl}_5-\text{AlCl}_3$ content in molten salts. And the metallothermic reaction was described as follows:



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2 Experimental

CaCl_2 , NaCl , LiCl , KCl , NbCl_5 , and AlCl_3 were all analytical reagents as solvent and raw materials, respectively. The pure metal sodium as reductant was used. In the $\text{LiCl-KCl-NaCl-CaCl}_2$ and LiCl-KCl-NaCl phase diagrams [17], the low eutectic point of these molten salt systems such as the LiCl-KCl-NaCl (54:36:10, mol%, abbreviated as LKN) and $\text{LiCl-KCl-NaCl-CaCl}_2$ (53:24:5:18, mol%, abbreviated as LKNC) was chosen.

Because the vapor pressure of NbCl_5 and AlCl_3 is very large at high temperature, NbCl_5 and AlCl_3 powder must have pre-treatment in molten salts. In this process, the mixed solvent of reagent in proportion was heated up slowly to 200 °C and dehydrated in vacuum for 6 h in a resistance furnace. After the reagent mixture was melted at 450 °C for 4 h under an argon (Ar) atmosphere, the LKN or LKNC molten salt was cooled to room temperature and milled to powders in the glove box under an argon atmosphere. Secondly, $3\text{NbCl}_5\text{-AlCl}_3$ mixture powders mixed with blank molten salts were placed inside a sealed quartz reactor in the glove box, after the reactor was quick placed into a 450 °C resistance furnace for 1 h, it was quick took out at room temperature, and the $\text{LKN-NbCl}_5\text{-AlCl}_3$ (96:3:1, mol%, abbreviated as LKNBA) or $\text{LKNC-NbCl}_5\text{-AlCl}_3$ (96:3:1, mol%, abbreviated as LKNCBA) precursor particles were prepared. Also, the small particles were cut from pure metal sodium ingot in the glove box for reduction. Finally, the LKN or LKNC blank molten salts were put into a corundum crucible which was placed inside a resistance furnace under an argon atmosphere and melted at 450 °C for 1 h. And then, the pre-treated precursor particles and the sodium particles (20 % excess) were fed into salt-bath for chemical reaction. After reaction, the

products and salts were cooled, washed, and dried in vacuum; the as-prepared products were obtained referred to our previous work [12–14].

The composition and microstructure of as-prepared products were determined by X-ray diffractometer (XRD, MAC Science Co. Ltd., M21X) with $\text{Cu K}\alpha$ radiation, field emission scanning electron microscopy (FESEM, ZIISS, ULTRA55, Germany) with an energy dispersive spectrometer (EDS, XMAX50, England), and transmission electron microscopy (TEM, JEM-2010, JEOL Co., Japan), respectively.

3 Results and discussion

3.1 Controlling homogeneous reaction system

3.1.1 Feeding material order effects

The XRD patterns of the as-prepared powders by chemical reduction of $3\text{NbCl}_5\text{-AlCl}_3$ with 20 % excessive sodium at 450 °C for 4 h in LKN molten salts are shown in Fig. 1. For $\text{Na} \rightarrow \text{precursor} \rightarrow \text{Na}$ order, Nb particles with a large amount of NbAl_3 and Nb_2Al are obtained, as shown in Fig. 1a. For $\text{precursor} \rightarrow \text{Na} \rightarrow \text{precursor}$ order, Nb_3Al powders are obtained, as shown in Fig. 1b. In addition, the morphology and EDS analysis of the obtained Nb_3Al products are shown in Fig. 2. The particle size distribution of Nb_3Al nanoparticles is 30–150 nm as shown in Fig. 2a. The majority elements of product nanoparticles are niobium and aluminum with a trace amount of oxygen by EDS element analysis, as shown in Fig. 2b. Nb/Al/O content in as-prepared Nb_3Al nanoparticles is evaluated to be 77.16 mol%/20.91 mol%/1.93 mol%. The molar ratio of Nb/Al in

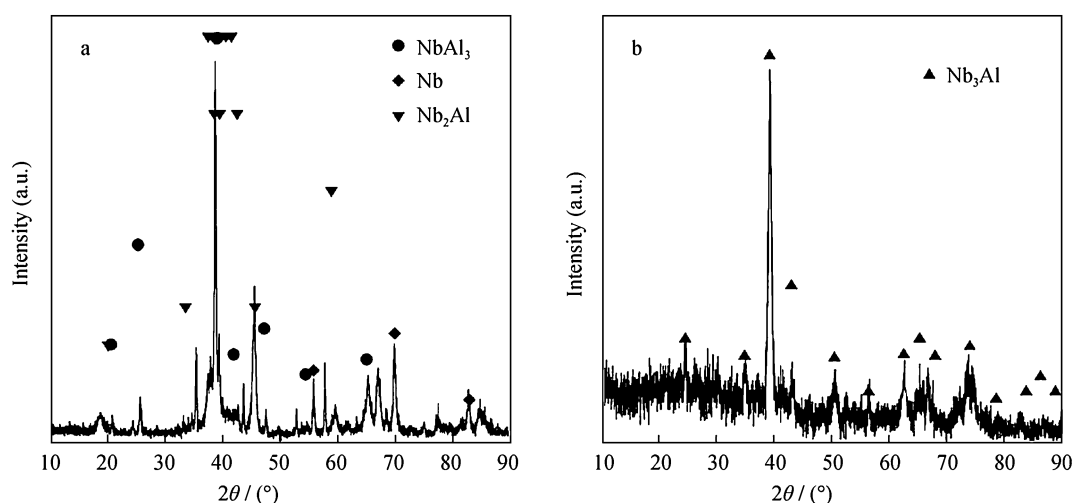


Fig. 1 XRD patterns of Nb_3Al powders from $3\text{NbCl}_5 + \text{AlCl}_3$ with different feeding material orders: **a** $\text{Na} \rightarrow \text{precursor} \rightarrow \text{Na}$ and **b** $\text{precursor} \rightarrow \text{Na} \rightarrow \text{precursor}$

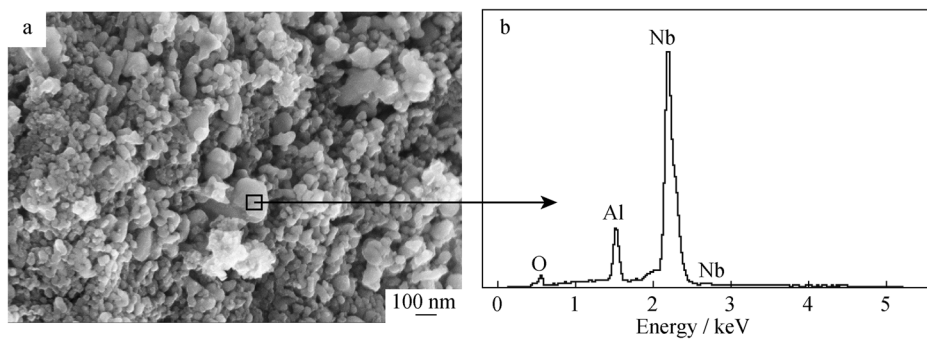


Fig. 2 FESEM image **a** and EDS spectrum **b** of Nb₃Al powders in LNKBA molten salts

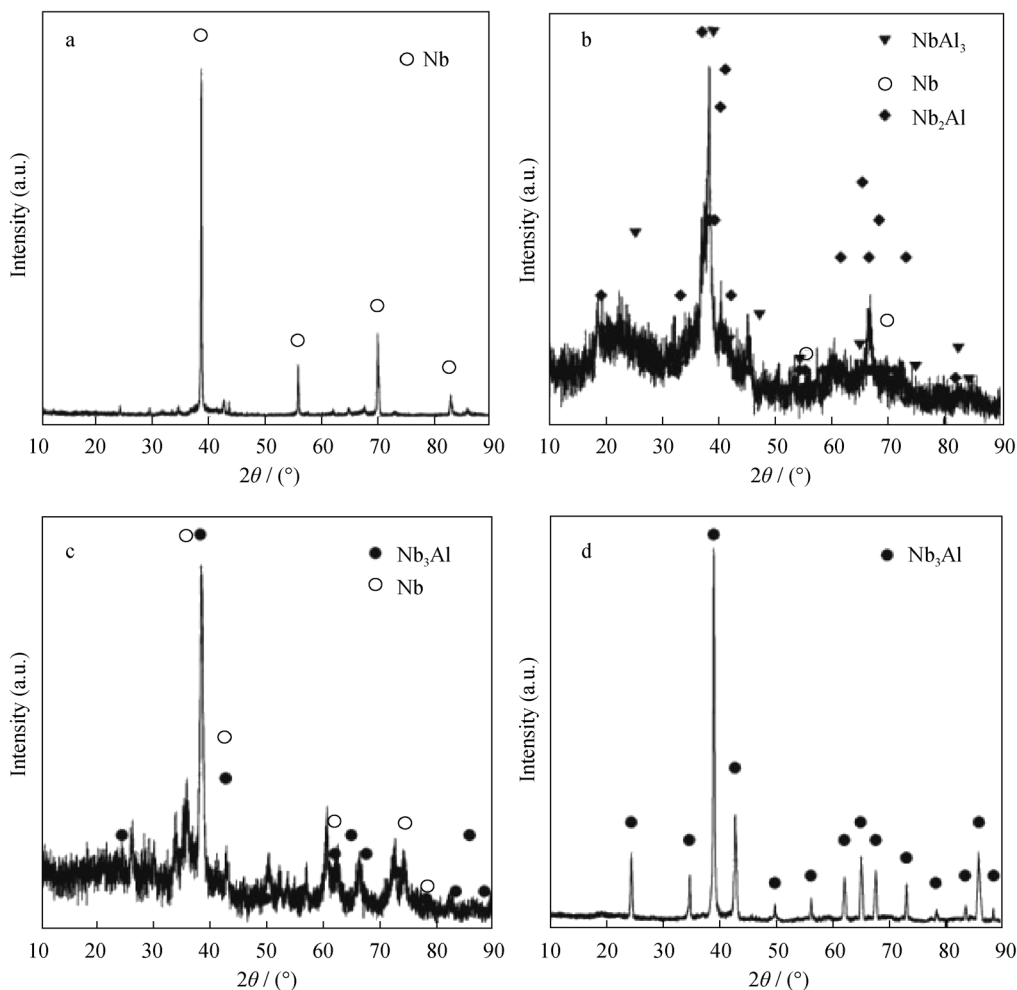


Fig. 3 XRD patterns of as-prepared powders for different soaking time: **a** 0.5 h, **b** 1.0 h, **c** 2.0 h, and **d** 3.0 h

the products is consistent with data in Nb–Al phase diagram [18].

According to the experimental results in LKNBA reaction systems, the feeding precursor particle and

sodium particle (20 % excess) orders are important to prepare pure Nb₃Al nanoparticles via chemical reduction process from NbCl₅ and AlCl₃ powders by sodium in molten salts.

3.1.2 Soaking time effects

Figure 3 shows XRD patterns of as-prepared powders by reducing $3\text{NbCl}_5\text{-AlCl}_3$ with sodium for different soaking time at $450\text{ }^\circ\text{C}$ in LKNC molten salts. After soaking for 0.5 h, Nb particles without Nb_3Al are obtained, as shown in Fig. 3a. After 1.0 h, the as-prepared Nb nanoparticles with a large amount of NbAl_3 and Nb_2Al are obtained as shown in Fig. 3b. With the increase in soaking time from 1.0 to 3.0 h, Nb, NbAl_3 , and Nb_2Al disappear and Nb_3Al nanoparticles without any impurity are obtained, as shown in Fig. 3c, d. In addition, FESEM and TEM images, EDS spectrum, and diffraction pattern of as-prepared products are shown in Fig. 4 (referred to Ref. [16]). The FESEM and TEM images of as-prepared powders are shown in Fig. 4a, c, respectively. Figure 4a, c shows that the particle sizes of pure Nb_3Al nanoparticles are about 50–200 and 90–180 nm, respectively. And the content of Nb/Al/O element in as-prepared particles is 91.58 wt%/6.43 wt%/1.99 wt%, as shown in Fig. 4b. Moreover, as presented in Fig. 4d, TEM image of Nb_3Al nanoparticles illustrates that the as-prepared particles are polycrystalline powders. Therefore, the optimum soaking time on LKNCBA

reaction system plays an important role in the formation of pure Nb_3Al powders in molten salts.

The above results demonstrate that only Nb_3Al nanoparticles without any impurity are obtained when LKNBA and LKNCBA molten salts form a homogeneous reaction system, which may be ascribed to the fact that all Nb and Al ions diffuse into reaction molten salt system and form a liquid phase. Thus, the optimum feeding raw material orders and soaking time play important roles in the formation of pure Nb_3Al particles in molten salts.

3.2 Controlling Nb content of products

Figure 5 shows Nb–Al phase diagram [18], and only Nb_3Al phase exists in Nb content of 77.5 mol%–82.0 mol% area. Therefore, controlling Nb content in raw materials is important to synthesize and obtain pure Nb_3Al nanoparticles. Figure 6 shows XRD patterns of as-prepared powders with Nb content in raw materials changing from 72 mol% to 85 mol% by stoichiometric ratio at $450\text{ }^\circ\text{C}$ in LKNCBA homogeneous reaction system. In the case of 85 mol% Nb, the Nb_3Al powders with a small amount of Nb phase were synthesized, as shown in Fig. 6a. With Nb content

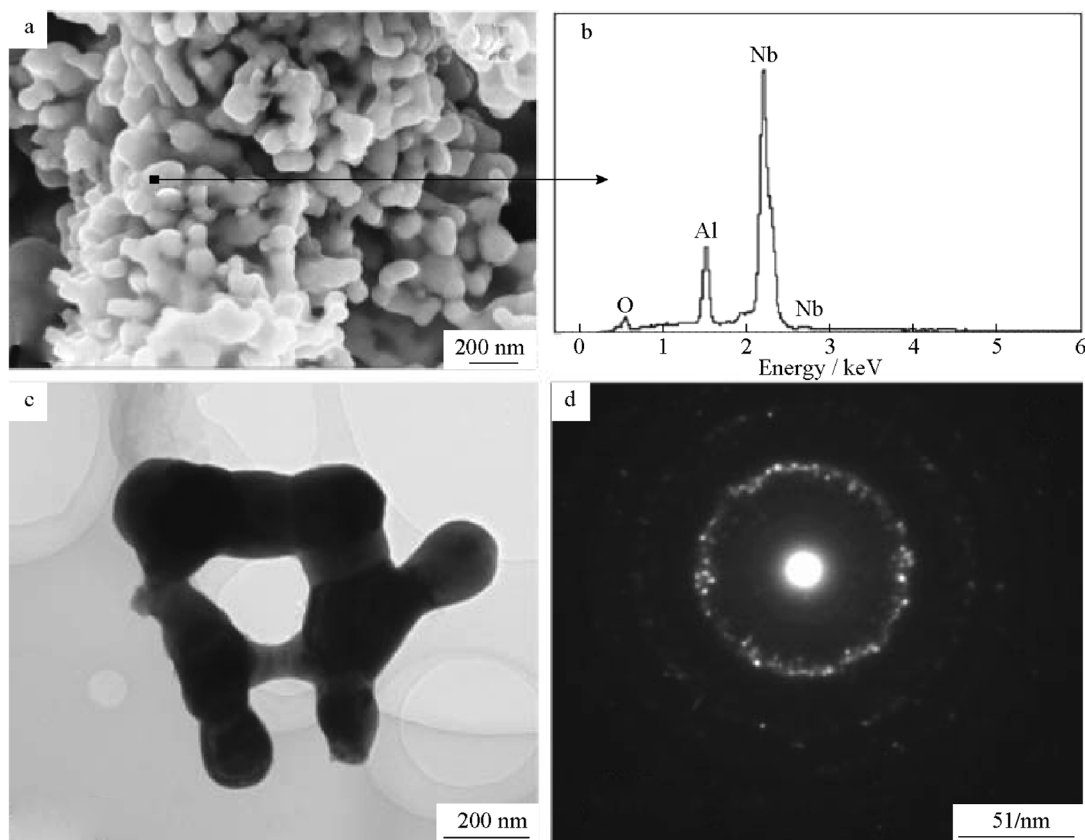


Fig. 4 FESEM image for EDS analysis **a** EDS spectrum **b** TEM image **c** and diffraction pattern **d** of Nb_3Al powders with soaking time of 3.0 h

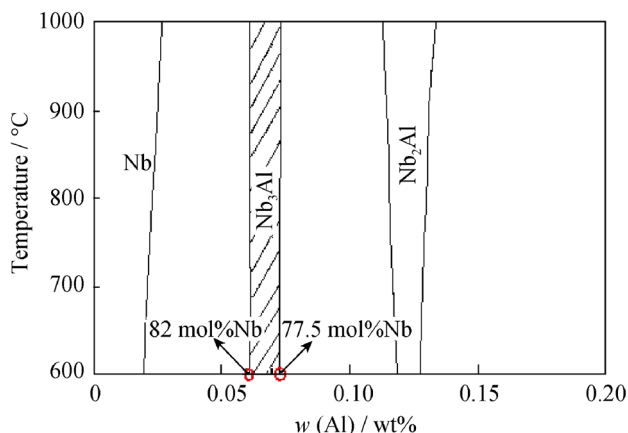


Fig. 5 Topical binary phase diagram of Nb–Al system

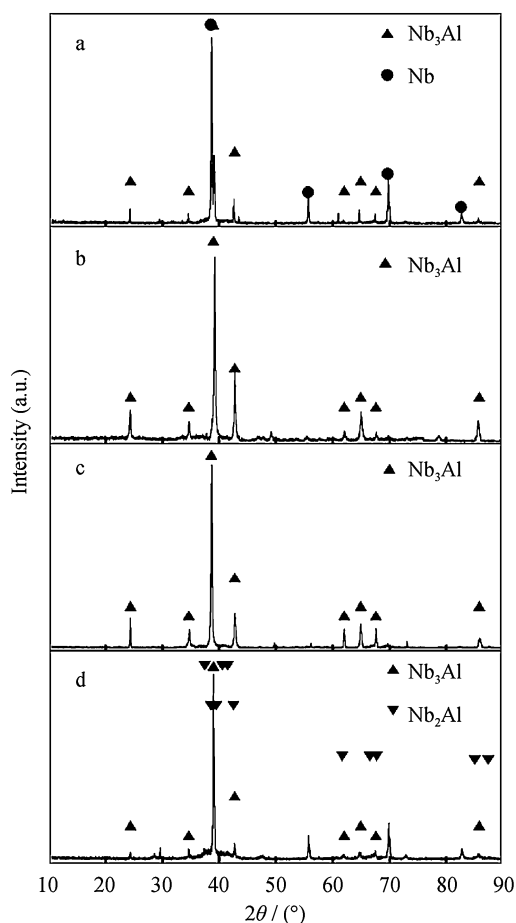


Fig. 6 XRD patterns of as-prepared Nb₃Al powders with different Nb contents in raw materials: **a** 85 mol%, **b** 82 mol%, **c** 78 mol%, and **d** 72 mol%

decreasing, the content of Nb phase decreases and Nb₂Al phase appears, as shown in Fig. 6. Pure Nb₃Al nanoparticles without any impurity are obtained, as shown in Fig. 6b, c. As-prepared Nb₃Al nanoparticles with a small

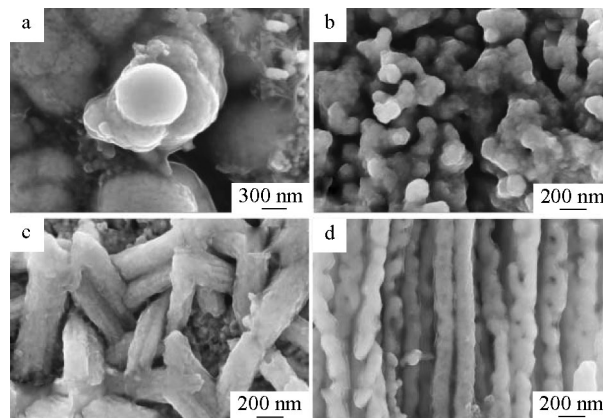


Fig. 7 FESEM images of Nb₃Al powders with different 3NbCl₅ + AlCl₃ contents: **a** 15 wt%, **b** 10 wt%, **c** 5 wt%, and **d** 2 wt%

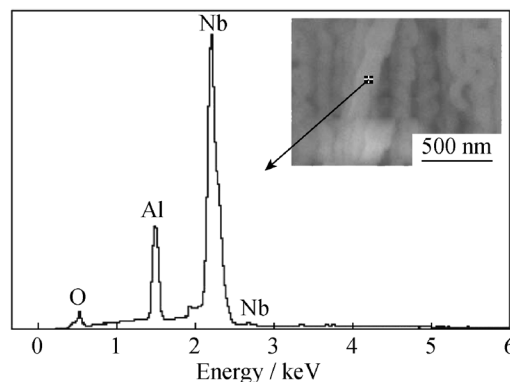


Fig. 8 EDS spectrum of Nb₃Al powders with 3NbCl₅ + AlCl₃ content of 2 wt% and inset being FESEM image for EDS analysis

amount of Nb₂Al are obtained, as shown in Fig. 6d. In addition, the formation of Nb₃Al nanoparticles in the reduction process is related to Nb content in raw materials (78 mol%–82 mol%). Therefore, it is necessary to conduct at the optimum amount of Nb ion in raw materials in the homogeneous reaction system.

3.3 Controlling morphology of products

FESEM images of as-prepared Nb₃Al powders by sodio-thermic reduction with different 3NbCl₅–AlCl₃ contents and 20 % excessive sodium at 450 °C in LKNC molten salts are shown in Fig. 7. For 3NbCl₅–AlCl₃ content of 15 wt%, as-prepared globular-like Nb₃Al nanoparticles are obtained, and the particle size distribution of pure Nb₃Al nanoparticles is 450–1200 nm as shown in Fig. 7a. With the content of 3NbCl₅–AlCl₃ decreasing from 15 wt% to 2 wt%, the particle size of Nb₃Al nanoparticles sharply decreases and the morphology of as-prepared Nb₃Al nanoparticles changes from globular-like to fine

filamentary, as shown in Fig. 7b–d. The fine filamentary Nb₃Al nanoparticles of as-prepared Nb₃Al powders, as shown in Fig. 7d, have diameters of 100–200 nm and length of 500–1600 nm. In addition, the EDS analysis of the obtained fine filamentary Nb₃Al nanoparticles is shown in Fig. 8. The content of Nb/Al/O element in as-prepared particles is 92.21 wt%/6.44 wt%/1.35 wt%, and the weight ratio of Nb/Al in the products is consistent with the data in Nb–Al phase diagram [18]. The above results demonstrate that various morphologies of as-prepared Nb₃Al powders without any impurity are obtained when the mixture raw material powder content in LKNCBA reaction system changes. Thus, the optimum content of raw materials in the LKNCBA reaction system plays an important role in the formation of Nb₃Al powders with different morphologies in molten salts.

4 Conclusion

The pure Nb₃Al nanoparticles could be successfully produced via chemical reaction in molten salts. It is found that controlling homogeneous reaction system and Nb content in raw materials is a very important operation for the formation of pure Nb₃Al product, that is, if the LKNBA and LKNCBA molten salts are not homogeneous reaction system, the pure Nb₃Al nanoparticles cannot be prepared. The morphology of as-prepared powders would change when the raw mixture material content in the homogeneous reaction system is different. Based on the experimental results, it is observed that via the precursor → Na → precursor order and soaking time of >3 h by chemical reaction in the molten salts with 78 mol%–82 mol% Nb in raw materials, single pure Nb₃Al nanoparticles can be prepared well.

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