



Effects of manganese and nickel addition on the preparation of niobium oxynitrides

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Abstract

Niobium oxynitrides were prepared by ammonolysis of the amorphous oxide precursors, obtained via citrate gelation, containing either a Mn or Ni additive. The product at 1000 °C, even with only 3 at% Ni, was a mixture of ϵ - and TiS-type Nb(N,O), containing a small amount of Ni metal impurity. Mn-containing products were δ -type (Nb,Mn)(N,O) with a NaCl structure. Upon post-annealing under a 0.2 MPa N₂ atmosphere at 1500 °C, the crystallinity of the δ -phase improved. The local structure around the substituted Mn²⁺ was greatly distorted with respect to the regular octahedral site in a δ -type crystal lattice. The microstructure of the post-annealed products containing Mn, as revealed by SEM observation, pointed to the appearance of a liquid phase. The superconductivity ($T_c = 15$ K) of δ -Nb(N,O) gradually vanished in δ -(Nb,Mn)(N,O), with increasing Mn amount above 5 at% Mn.

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1. Introduction

Niobium nitrides are known to form the ϵ -NbN phase with a TiP-type structure below 1300 °C and the superconducting δ -NbN phase with a NaCl-type structure above 1450 °C ($T_c = 17.2$ K).^{1,2} NbN thin films have been fabricated to exploit the material's superconductivity in Josephson junctions.³ The superconducting transition temperature, T_c , varied between 2 and 18 K by forming a δ -(Nb, M)N solid solution (M = Ti, V, Zr, Hf, Ta) to change the Fermi level in the rock-salt-type lattice.^{4,5} Niobium oxynitrides such as δ - and ϵ -Nb(N, O) isostructural to the nitrides have been identified.⁶

Recently, we synthesized three kinds of partially substituted niobium oxynitride superconductors: (Nb_{0.89}Al_{0.11})(N_{0.84}O_{0.16}), (Nb_{0.95}Mg_{0.05})(N_{0.92}O_{0.08}), and (Nb_{0.87}Si_{0.09}□_{0.04})(N_{0.87}O_{0.13}) with a T_c of around 17 K.^{7–9} Silicon was doped with a high density of cationic vacancies to maintain charge neutrality in the niobium oxynitride lattice with a NaCl-type structure. The position of silicon was slightly shifted from a

regular octahedral site toward a tetrahedral site in the crystal lattice. The distorted local structure served as a flux pinning center for superconductivity. The estimated J_C at 5 K for the Si-doped sample was $\sim 2.5 \times 10^4$ A/cm² under a magnetic field of 1 T and for an average grain dimension of 0.01 cm.¹⁰ The superconducting state of (Nb_{0.87}Si_{0.09}□_{0.04})(N_{0.87}O_{0.13}) was very recently studied using muon spin rotation and relaxation. The Uemura plot of the niobium oxynitride suggested that the mechanism for superconductivity may not be entirely conventional, but rather, resemble those in cuprates, organics, and heavy fermion systems.¹¹

Several niobium oxynitrides with different types of structure have been reported in preparations containing Mn below 900 °C. Both Nb_{3.49}(N_{4.56}O_{0.44}) and (Mn_{0.54}Nb_{3.07})(N_{4.40}O_{0.60}) of the Nb₄N₅ type are presumed to be NaCl-type □^{2a}Nb^{8h}₄N₅ with an ordered cationic vacancy at 750 °C. Cubic (Nb, Mn)(N,O) of the NaCl type was observed at 900 °C along with MnNb₂(N,O)₃ of a hexagonal Nb₅(N,O)₆ related crystal structure having three kinds of cationic sites: trigonal 6g site occupied by only Nb, octahedral 4d site occupied by roughly equal amounts of Mn and Nb, and the octahedral 2b site occupied by Mn alone.¹² Hexagonal oxynitride (Li_{0.88}□_{0.12})Nb₃(O_{0.13}N_{0.87})₄ was synthesized through ammonolysis of LiNb₃O₈ and showed superconductivity below 3 K.¹³ Hexagonal Nb₅(N,O)₆ was also obtained with

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$\text{Nb}_4(\text{N},\text{O})_5$ impurity in the preparation containing 11 at% Co at 750 °C. Hexagonal $\text{Nb}_5(\text{N},\text{O})_6$ was similarly prepared with Fe_2N and FeO impurities.^{12,14} The niobium oxynitride crystal lattice contained neither cobalt nor nickel. The thermal behavior varies depending on the kinds of coexisting transition metals. The transition metals' chemical bonds with nitrogen in transition metal nitrides gradually became unstable, owing to the increasing antibonding contribution of an increasing number of 3d electrons.¹⁵ Their difference in chemical stability may introduce the variation of defect structure useful for its superconductivity in niobium oxynitride crystal lattice. The thermal behavior of Mn-doped niobium oxynitride is not yet known at temperatures above 1000 °C. These data are needed to understand in what type of local structure around Mn occurs in the superconducting δ -NbN. Oxynitrides show a rich set of characteristics similar to those of the abovementioned $(\text{Nb},\text{Si})(\text{N},\text{O})$ forming a useful nanometer- to micrometer-sized structure as a flux pinning center for superconductivity.^{7–11} Another example of shaping at the nanoscale is gallium oxynitride nanowire formation. It has been demonstrated that anisotropic crystal growth is induced by the thermal metastability of the bonds between nitrogen and doped Co or Ni in a nitride crystal lattice.^{16–18}

In the present investigation, niobium oxynitrides were prepared, using a Mn or Ni as additive with much different stability, by ammonolysis at 1000 °C of oxide precursors obtained via citrate gelation at the optimized firing temperature. Post-annealing was performed under a 0.2 MPa N_2 atmosphere at 1500 °C for 3 h. The crystalline phases that appeared were studied by powder XRD, and the local structure around Nb and Mn was investigated by X-ray absorption spectroscopy. The microstructure of the sintered bodies was characterized by SEM–EDX. Superconductivity was measured by a SQUID magnetometer.

2. Experimental

Amorphous oxide precursors were obtained by the following method: NbCl_5 (Sigma-Aldrich, 99.9%) was dissolved with either $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Kanto Chemicals Co. Inc., 99%) or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Kanto Chemical Co. Inc., 98%) up to 10 at% in 20 mL of anhydrous ethanol. An equimolar amount of citric acid (Wako Pure Chemical Industries Ltd., 98%) was added as a complexing agent. The viscous product was fired at various temperatures for 20 h in air, and the resultant amorphous oxide powders were ground. Residual carbon was present at 350 °C, and the oxides crystallized slightly at 600 °C. The amorphous precursors at 400 °C containing no residual carbon were nitrided in alumina boats under an ammonia (Sumitomo Seika Chemicals, 99.9%) flow of 50 mL/min at 1000 °C for 10 h. After the ammonolysis reaction, the samples were cooled to room temperature, and the residual ammonia in the silica glass reaction tube was purged by a nitrogen gas flow. Each as-nitrided product was thermally annealed on a thin pellet of the same nitride in a BN crucible at 1500 °C for 3 h under 0.2 MPa N_2 in a graphite furnace (High Multi 5000, Fuji Dempa Kogyo).

The as-nitrided and post-annealed products were characterized by using X-ray diffraction (XRD) and magnetic

measurements. XRD patterns were collected using a diffractometer (Ultima IV, Rigaku) with monochromatized $\text{Cu K}\alpha$ radiation over a 2θ range of 10–80° with a step size of 0.02°. Magnetic susceptibility was measured using a SQUID magnetometer (MPMS-5S, Quantum Design) between 2 and 20 K under a magnetic field of 5 mT. The magnetic field dependence of the annealed products was measured between –5 T and 5 T at 5 K. Both Mn and Nb K-edge X-ray absorption spectra were measured in the transmission mode at beamlines 9C and NW-10A, respectively, at the Photon Factory, High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The spectrum was analyzed using the software REX2000 (Rigaku) with $n=3$ in the k -range of 0.30–0.80 nm.¹⁹ The microstructure of the surface of the annealed ceramics was characterized by SEM (JSM 6390LV, JEOL).

3. Results and discussion

The oxide precursors were amorphous after firing in air at 400 °C in the cases of both 3 at% Ni and 3 at% Mn. A slight crystallization of NiO impurity appeared in the precursor at 10 at% Ni. The amorphous oxide precursors were nitrided in flowing NH_3 at 1000 °C. The additive-free nitrided product was mainly ε -Nb(N,O), mixed with some TiS-type Nb(N,O), as shown in Fig. 1(a). The crystal structure of TiS-type NbN has been known to be in between δ' - and δ -NbN with an anti-NiAs- and NaCl-type structure, respectively.²⁰ A small amount of Ni metal occurred on the nitrided product containing 3 at% Ni together with the δ' -phase in the mixture similar to ε - and TiS–Nb(N,O) as seen in Fig. 1(b). The crystallization behavior of the Mn-doped products up to 10 at% Mn differed greatly from

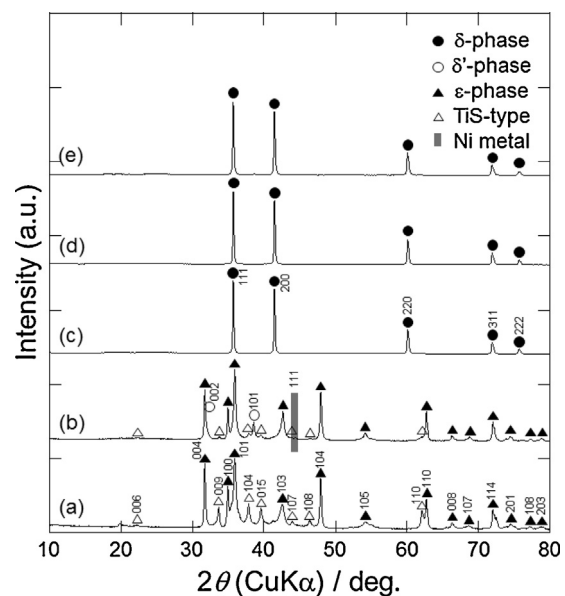


Fig. 1. X-ray diffraction patterns of the ammonolysis products at 1000 °C prepared from (a) amorphous niobium oxide, (b) 3 at% Ni-, (c) 3 at% Mn-, (d) 5 at% Mn-, and (e) 10 at% Mn-containing niobium oxides. Filled and open circles are the diffraction peaks for the δ - and δ' -phases; filled and open triangles are those for ε - and TiS-type phases, respectively. A trace amount of nickel metal appeared at the hatched diffraction angle.

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