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Processes to produce superconducting Nb_3Sn powders from Nb–Sn oxide

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The superconducting compound Nb_3Sn was produced by the reduction of the oxides or hydroxides of niobium and tin. The procedure consists of the following three steps; (i) preparation of the mixed oxides or hydroxides, (ii) direct alloy reduction, and (iii) homogenizing heat treatment of the reduced metal powders. For mixing the two oxides, two methods were tried: the simultaneous precipitation from the aqueous solution and the solidification of the molten oxides. These mixed oxides were reduced by calcium or magnesium vapour in the temperature range 973 to 1373 K. After calcium or magnesium oxide was removed by leaching the fine compound powder had an A-15 type crystal structure, but showed a relatively low superconducting critical temperature (T_c). The final isothermal annealing improved T_c to 18.0 K.

1. Introduction

The intermetallic compound Nb_3Sn is gathering attention as a valuable superconducting material for practical use, and many attempts have been made to prepare the stoichiometric Nb_3Sn. The practical superconducting Nb_3Sn wires have recently been produced by using the diffusion of tin from Cu–Sn alloy (bronze) into niobium wires, by the so-called bronze process [1]. By this process a very thin layer of Nb_3Sn can be formed at the interface between niobium cores and the Cu–Sn matrix. To prepare a large amount of pure Nb_3Sn, other methods are required. The significant evaporation of tin above the melting point of niobium, however, leads to difficulties in mixing accurately liquid niobium with tin [2]. Because the sintering of niobium and tin powders at the lower temperatures tends to form the intermetallic compound Nb_6Sn_5 and/or $NbSn_2$ in addition to Nb_3Sn, the homogeneous and pure Nb_3Sn single phase with a fine grain size cannot be easily obtained by powder metallurgy [3, 4].

This paper reports a new method to produce the superconducting Nb_3Sn powders by the co-reduction process. Fig. 1 shows the procedure of the present method. An oxide mixture solidified from the homogeneous melt of Nb_2O_5 and SnO_2 or a hydroxide mixture homogeneously precipitated from the aqueous solution containing niobium and tin cations was employed as the starting material. These mixed oxides or the simultaneous precipitates were then reduced by a strong reducing agent (calcium or magnesium) between 973 and 1373 K. Subsequently, the heat treatment of the reduced Nb_3Sn powder was made to improve the superconducting properties.

2. Experimental details

2.1. Preparation of oxides or hydroxides mixtures

As described above, the simultaneous precipitation technique was applied in this study to prepare the mixture of hydroxides of niobium and tin. This technique had been used in preparing a powder of complex ferrite ($(MFe_2)O_4$, M = transition metals) with a very fine grain size [5, 6]. A total of about 10g high-purity niobium pentachloride ($NbCl_5$) and tin (II) chloride ($SnCl_2\,2H_2O$) at a Sn/Nb ratio of 1/3 was dissolved in 50 ml concentrated hydrochloric acid solution. This solution was dropped into 100 m aqueous ammonium solution, where the pH of the neutralized solution was controlled between 6 and 9. The residual concentration of niobium and tin ions in the solution were calculated to be less than $10^{-8}\,\mathrm{mol\,dm^{-3}}$ [7], and the residual ions could not be detected experimentally. After separation of the precipitates from the solution by centrifugation, the ammonium chloride adhering to the precipitates was removed by washing it several times with deionized water. The yellow-coloured cake of dried precipitate was ground into a powder.

The phase diagram of niobium pentaoxide (Nb_2O_5) and tin (IV) oxide (SnO_2) shows a simple eutectic reaction with a eutectic point of 1750 K at Nb_2O_5–10 mol % SnO_2, and the liquidus temperature of the composition at Sn/Nb = 1/3 is about 1815 K [8]. For the preparation of the mixed oxides, Nb_2O_5 and SnO_2 powders of 99.95 and 99.5% purity, respectively, were melted in a platinum crucible in air at around 1873 K and rapidly solidified on the water-cooled copper plate.

2.2. Reduction by calcium and magnesium

For the reduction of niobium and tin oxides by a metal element, the following terms may be needed: (i) a standard free energy of formation of the oxide lower than that of niobium and tin oxides, (ii) a reducing agent that does not form an alloy with niobium and tin, (iii) the easy removal of the oxide of the reducing agent formed after reduction, (iv) a relatively fast reduction at lower temperatures, and (v) a reasonable cost. Table I shows the standard free energies of the formation of the oxides for some elements [9–11]. Calcium and magnesium were selected as possible reducing elements for the reason mentioned above.

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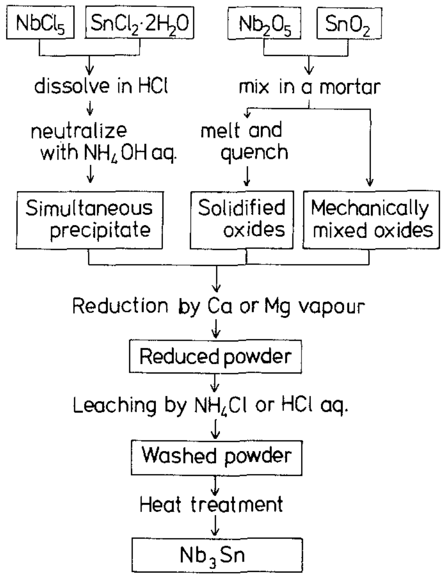


Figure 1 Processes to form Nb_3Sn. There are three choices as the starting material for the reduction.

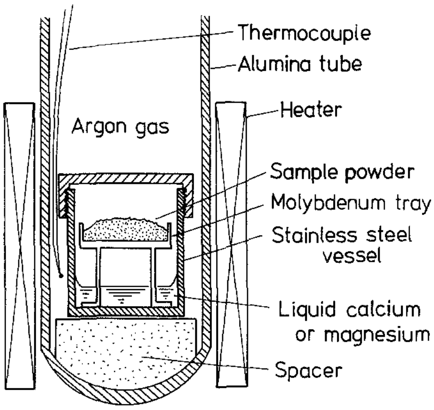


Figure 2 Apparatus for the reduction by calcium or magnesium vapour.

Calcium and magnesium both have relatively low melting points, 1112 K and 922 K, respectively, and their equilibrium vapour pressures in the liquid state are high enough [11] to reduce both niobium and tin oxides by their vapour. The reduction by the vapour was thought to be more favourable than that by the solid or liquid for acceleration of the reaction, for less contamination by impurities in the reducing agent, and for decrease of the residual amount of the excessive reducing agent attached to the specimen.

Fig. 2 illustrates the experimental apparatus used for the reduction. The reducing agent was laid in the bottom of the vessel which was made of stainless steel. About 5 g hydroxide powder or the solidified oxides was placed on the molybdenum disc in the vessel. The calcium and magnesium used in this study had a purity of about 98%, and their oxides were main impurity. The charged amount was two or three times the stoichiometric one, taking account of leakage of the vapour. The vessel set up in the alumina tube was evacuated and heated to about 800 K for dehydration, and heated further up to a reduction temperature in the purified argon atmosphere. After a given holding time, it was cooled in the furnace. In this work the reduction temperatures were chosen so that the vapour pressure [11] did not exceed a few tens kPa because the reducing gas leaked out of the reaction vessel at higher vapour pressure.

TABLE I Standard Gibbs free energies for the formation of the oxides (ΔG^0) after [10–11] where $\Delta G^0 = RT \ln P_{O_2}$ (R = gas constant, P_{O_2} = equilibrium oxygen partial pressure)

Element	Oxide	Gibbs free energy, ΔG^0 (kJ mol O$_2$)		
		1073 K	1273 K	1473 K
Sn	SnO$_2$	−355	−312	−269
C*	CO	−461	−441	−422
H*	H$_2$O	−459	−452	−444
Nb	NbO	−642	−611	−581
Si	SiO$_2$	−716	−681	−646
Ti	TiO	−832	−797	−761
Al	Al$_2$O$_3$	−890	−846	−802
Zr	ZrO$_2$	−881	−843	−807
Ba	BaO	−924	−880	−835
Mg	MgO	−981	−973	−874†
Be	BeO	−994	−957	−919
Ca	CaO	−1054	−1012	−969
Th	ThO$_2$	−1069	−1000	−965

*Supposing $P_{CO}/P_{CO_2} = 10^2$ and $P_{H_2}/P_{H_2O} = 10^2$.
†Supposing P_{Mg} = 101 325 Pa.

The reduction of the mixed oxides by calcium, for instance, may be written as

$$(3Nb_2O_5 \cdot 2SnO_2) + 19Ca(gas) = 2(3Nb \cdot Sn) + 19CaO \quad (1)$$

$$3Nb \cdot Sn = Nb_3Sn \quad (2)$$

where the mixed oxides are deoxidized to metallic niobium and tin, and the Nb_3Sn compound is formed at the same time. The aqueous solution with 10 wt/vol % NH_4Cl (pH = 5) was used for the separation of calcium oxide. For the separation of magnesium oxide, the hydrochloric acid solution (pH = 1 to 2) was used for the reason stated later.

2.3. Heat treatments

The separated Nb_3Sn powder was pressed and annealed isothermally in an evacuated silica tube to complete the formation and homogenization of Nb_3Sn. Annealing was applied at temperatures between 873 and 1273 K.

2.4. Evaluation of some properties

The identification of the phases existing in the specimens and the lattice constant measurements of the Nb_3Sn phase were carried out by X-ray diffractometry, and the results were compared with JCPDS cards. X-ray microprobe analysis (XMA) was performed to obtain the compositional profiles on the cross-section of the hydroxides and the solidified oxides before reduction. The morphology and configuration of the powder were examined by scanning electron microscopy (SEM) without etching. The average particle size (d) is given by the equation, $d = 4L/\pi$, where L is the average length measured with the line-intercept method when each spherical grain is isolated. The superconducting property was evaluated by the critical temperature (T_c) using the inductance method [12–14], which was suitable for

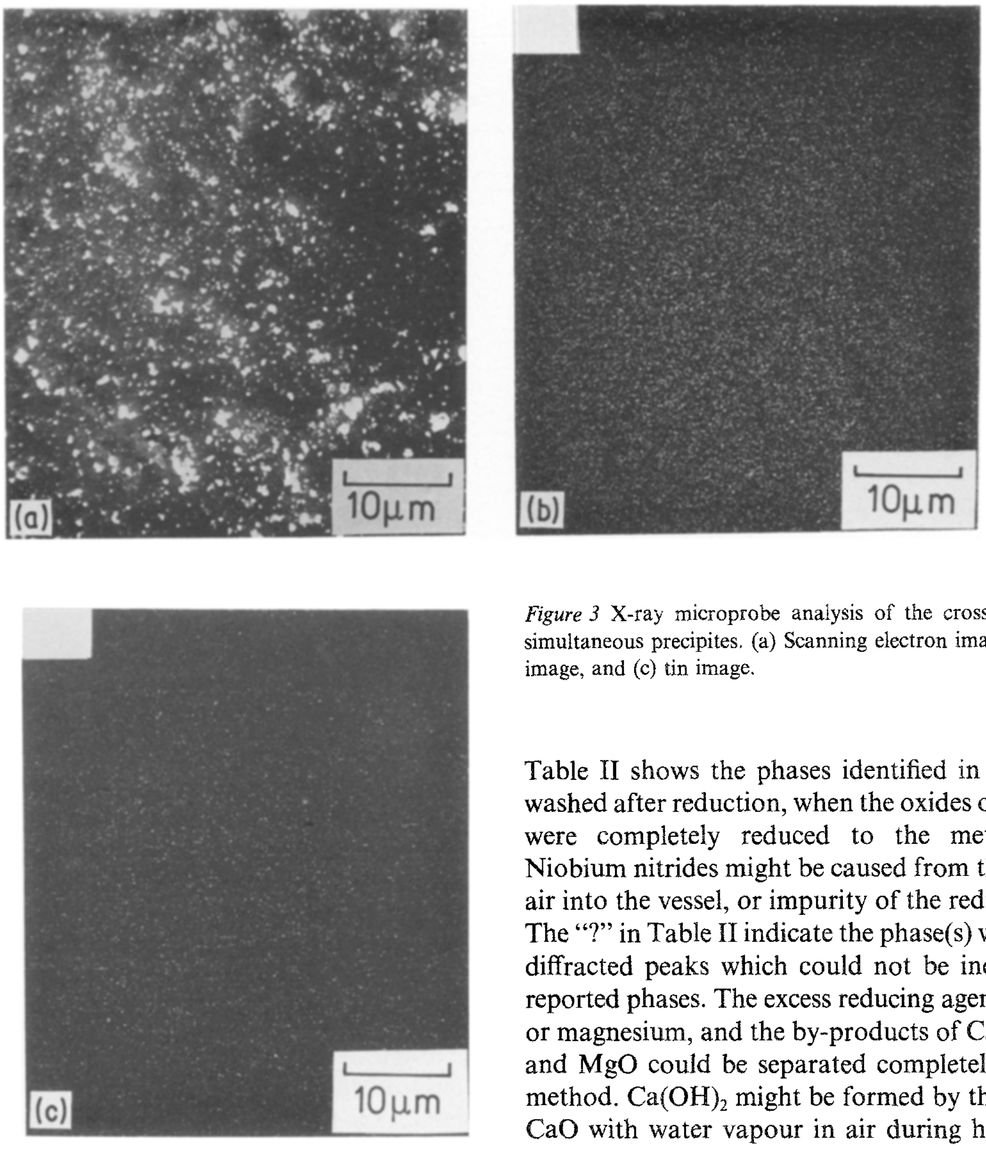


Figure 3 X-ray microprobe analysis of the cross section of the simultaneous precipites. (a) Scanning electron image, (b) niobium image, and (c) tin image.

the powdery specimen. T_c was defined as the offset value of inductance change [13, 14].

3. Results and discussion

3.1. Mixture of hydroxides and mixture of oxides

The cake of a dried precipitate containing niobium and tin was confirmed to be amorphous by X-ray diffraction measurements. Fig. 3 shows that niobium and tin atoms in the precipitates were dispersed homogeneously within the limit of resolution of XMA. This may be regarded as the mixture of niobium and tin hydroxides.

The rapidly solidified specimens containing Nb_2O_5 and SnO_2 with a Sn/Nb ratio of 1/3 were identified as the mixture of monoclinic Nb_2O_5 and tetragonal SnO_2 by X-ray diffraction measurements. These solidified oxides show the eutectic structure composed of the fine grains with a few micrometres, as shown in Fig. 4.

3.2. Reductions

The mixture of the hydroxides or the solidified oxides was ground to a fine powder of about 100 μm particle size, and reduced by calcium or magnesium. In this study, the reduction conditions were adopted by the combination of four factors as shown in Table II. Table II shows the phases identified in the powders washed after reduction, when the oxides or hydroxides were completely reduced to the metallic forms. Niobium nitrides might be caused from the leakage of air into the vessel, or impurity of the reducing agents. The "?" in Table II indicate the phase(s) with the weak diffracted peaks which could not be indexed by the reported phases. The excess reducing agents of calcium or magnesium, and the by-products of CaO, $Ca(OH)_2$ and MgO could be separated completely by the wet method. $Ca(OH)_2$ might be formed by the reaction of CaO with water vapour in air during handling after the reduction.

After the reduction by magnesium, X-ray diffraction measurements confirmed that the Nb_3Sn phase existed in all samples and the single phases of Nb_3Sn were obtained in a few conditions. The formation of the Nb_3Sn phase, however, was poor in the powders after reduction by calcium. No relationship between the reduction time and temperature, and no difference between the solidified oxides and hydroxide mixture as the starting material were found.

Note that when magnesium was used as the reducing agent, the compound Mg_2Sn was detected in the powders before washing, and part of the tin shown in Table II came from it. After the reduction by calcium, the powder did not contain any intermediate (transitional) phases. The fact that Mg_2Sn is liquid above 951 K [15] shows that the excess magnesium formed a liquid alloy with part of the reduced tin at the reducing temperature. This phenomenon indicates that tin oxide was reduced prior to niobium oxide, according to the standard free energy of formation of their oxides. This liquid Sn–Mg alloy, however, might not prevent the formation of the Nb_3Sn phase. Nb_6Sn_5 and $NbSn_2$, which suppressed the formation of Nb_3Sn in the synthesis from the pure elements, have been reported [1] not to be produced by the bronze process because the activity of tin was low in the Cu–Sn alloy. The low activity of tin in the liquid Mg–Sn alloy [16]

TABLE II Existing phases in the washed powders after reduction, which were determined by X-ray diffraction measurements

No.	Starting material	Reducing element	Temperature (K)	Reducing time (10^3 sec)	Identified Phases					
					Nb_3Sn	Nb	Sn	NbO	Nb_2N	?
I1	Hydroxides	Mg	973	86	◎	○	○		○	
I3			973	173	○		○		◎	
T2			973	310	◎					
F2			1073	86	◎	◎	○	△		
F3			1073	86	◎	◎	○	△		
O6			1073	86	◎	○			△	
O7			1073	144	◎	○				△
O8			1073	144	◎	◎	○		△	△
F1			1073	259	◎		○			
L1			1173	54	◎	◎	○		△	
K1			1173	86	◎	◎	○			△
T4			1173	162	○		◎			
V2			1173	259	◎		△		○	
P4	Solidified oxides	Mg	1073	259	◎		△			△
P5			1173	86	◎		◎			
P3			1173	259	◎					
P6			1273	86	○		○			○
D1	Hydroxides	Ca	1273	151		◎	◎	△	○	
D2			1273	144	○	◎	◎	◎	○	
R3			1273	173	○	△	◎		○	△
T1			1273	259		◎	◎			○
U5			1373	86	○	◎	◎			△
U2			1373	173		◎	◎			△
U4			1373	173		◎	◎		○	
U1			1373	346			◎		◎*	

The ratio of the relative intensities of the formed phases are weaker in this order; ◎, ○, and △.
*Sample U1 contained Nb_4N_3 and NbN in addition to Nb_2N.

is, therefore, presumed to prevent the synthesis of Nb_6Sn_5 and $NbSn_2$ in this study.

Mg_2Sn was completely soluble in the acid solution with pH < 0.5, while only magnesium preferentially dissolved in the acid solution with a pH of 0.5 to 3 and β-tin crystals were precipitated. Magnesium and its oxides, as well as Mg_2Sn, were difficult to dissolve in the acid solution with a pH higher than 4. The pH 1 hydrochloric acid solution was, therefore, adopted for the decomposition of Mg_2Sn and the extraction of magnesium. The elution of niobium and tin in this leaching treatment could not be detected by chemical analysis.

Figs 5a and b show the scanning electron micrographs of the powder reduced by calcium, before and after washing in NH_4Cl solution, respectively. Fig. 5a shows that calcium oxides covered the particles completely, while the fine isolated particles can be seen in Fig. 5b after the elimination of CaO. The grain (particle) refinement is considered to be caused by the reaction of the reducing agents, the formation of their oxides in the reduced powder, and the initiation and expansion of the cracks by their oxides causing a successively fresh reduction.

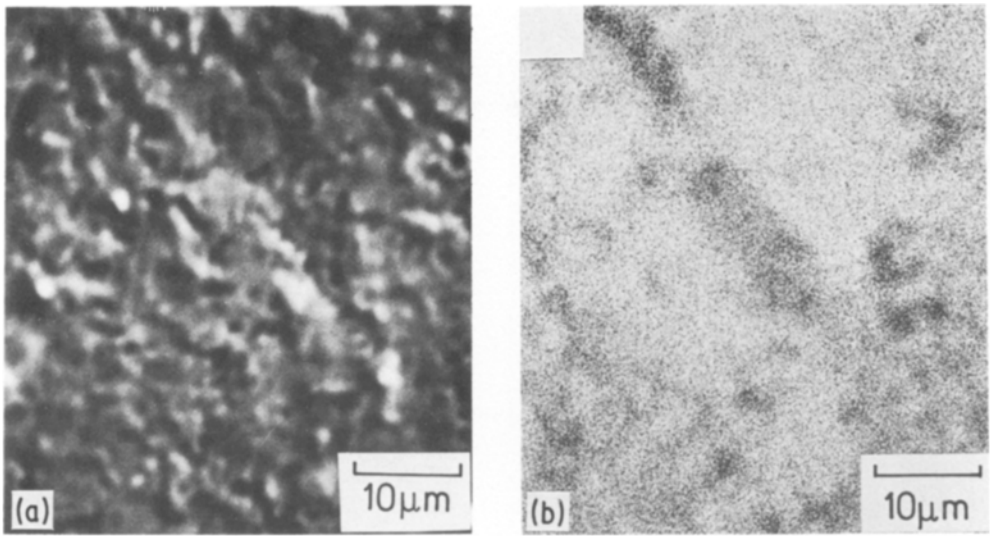
For comparison, Nb_2O_5 and SnO_2 were mechanically mixed in a mortar and were reduced by calcium or magnesium, whose particle size was about a few tens micrometres. They were reduced to metallic niobium and tin, but Nb_3Sn was not synthesized even after a long reduction time. SEM observations showed that the oxide film of the reducing agent completely covered each niobium and tin particle. This suggests that the Nb_2O_5 and SnO_2 particles were reduced independently and that the oxide film prevented the interdiffusion of each metallic element. Niobium and tin atoms in the hydroxides and the solidified oxides, however, adhered closely with each other and the atomic ratio of niobium and tin was maintained at 3 : 1 at least in a micrometre order. Thus Nb_3Sn could be formed even by local diffusion in the particles covered with the oxide film of the by-product.

3.3. Heat treatment and superconductivity

Isothermal annealing was applied to the washed powders after the separation of CaO or MgO. Table III shows the analysis of the metallographic investigations and the critical temperature of superconducting transition (T_c) for the as-washed powders and the heat-treated ones.

Fig. 6 shows the inductance change accompanied by the superconducting transition for the specimens isothermally annealed at 1273 K after the reduction by magnesium at 1173 K for 259 × 10^3 sec. T_c has so far been reported to be 18.0 to 18.1 K for the stoichiometric Nb_3Sn [1], but T_c was 9.1 K for this as-reduced powder which had the Nb_3Sn single phase, as shown in Table III. The facts that the inductance change below T_c for this specimen was not so sharp, that the lattice of this Nb_3Sn expanded as shown in Table II and that the X-ray diffracted peaks were broad, may suggest that many defects and inhomogeneities existed in the as-reduced Nb_3Sn phase and, therefore, niobium and tin atoms in this Nb_3Sn lattice could not be arranged in a chain structure adequate for the superconducting properties.

However, Fig. 6 shows that the isothermal annealing



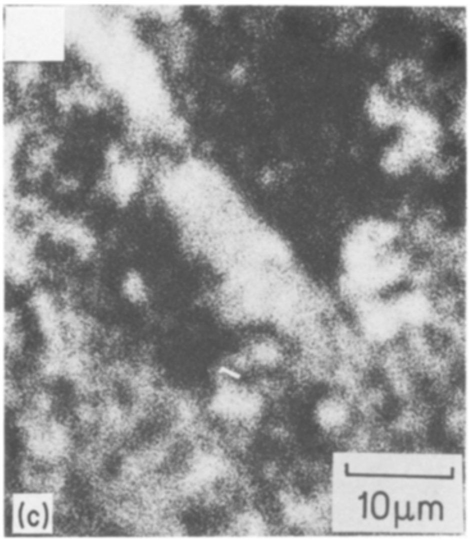


Figure 4 X-ray microprobe analysis of the cross section of the solidified oxides of Nb_2O_5 and SnO_2. (a) Scanning electron image, (b) niobium image, and (c) tin image.

at 1273 K elevated T_c and sharpened the inductance change below T_c, and the Nb_3Sn single phases with $T_c = 18.0$ K were formed by annealing for 86×10^3 sec.

It is necessary to have both a high critical magnetic field (H_c) and high critical current density (J_c) for the construction of a superconductor with a high current capacity [1]. For the superconducting compounds including Nb_3Sn to maintain these properties, the grain size should be as fine as possible. Recently, a grain size below 0.05 µm has been realized by using the bronze process [1, 17–20]. Supposing that the obtained particle size corresponds to the grain size because the fine structure inside the particle could not be observed in this work, the additional heat treatments were useless to improve the refinement of the grain size, as shown in Table III.

As shown in Table III, for instance, the as-reduced specimen by magnesium at 1073 K for 259×10^3 sec contained a small amount of tin in addition to Nb_3Sn, and its average particle size was relatively small (0.30 µm). The isothermal annealing could make this specimen the Nb_3Sn single phase with a T_c of 18.0 K, but the particle size was coarsened to 0.86 µm. Further

TABLE III Phases formed, lattice parameters (a_0) of Nb_3Sn, critical temperatures (T_c) and average particle sizes (d) for the as-reduced and isothermally annealed powders after the reduction by magnesium or calcium vapour

Reducing agent	Reducing condition	Heat treatment	Phases formed	a_0 (nm)	T_c (K)	d (µm)
Mg	1073 K 259×10^3 sec	As-reduced	Nb_3Sn, Sn	0.5295	< 4.2	0.30
		1273 K 605×10^3 sec	Nb_3Sn	0.5290	18.1	0.86
	1173 K 259×10^3 sec	As-reduced	Nb_3Sn	0.5294	9.1	1.0
		1273 K 605×10^3 sec	Nb_3Sn	0.5289	18.0	1.3
Ca	1273 K 173×10^3 sec	As-reduced	Nb, Sn, NbO, Nb_3Sn, Nb_2N, ?	–	–	0.41
		873 K 680×10^3 sec	Nb_6Sn_5, Nb_2N, Nb_3Sn, Nb, NbO	0.5288	9.7	0.38
		1273 K 605×10^3 sec	Nb_3Sn, NbO, Nb_2N	0.5289	18.1	0.82
	1273 K 151×10^3 sec	As-reduced	Nb, Sn, NbO, Nb_2N	–	–	0.44
		1073 K 680×10^3 sec	Nb_3Sn, NbO, Nb_2N	0.5298	17.3	0.40

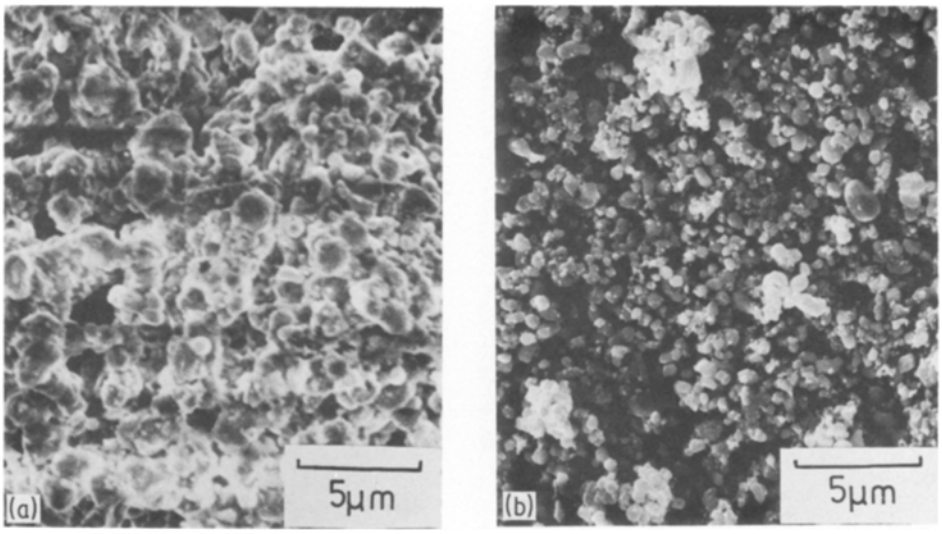


Figure 5 Scanning electron micrographs of the reduced powders by calcium at 1273 K for 82 × 10^3 sec. (a) before washing, (b) after washing by 10 wt/vol % NH_4Cl solution.

studies on the heat treatment are needed to maintain a fine particle size when the synthesis to Nb_3Sn is completed from the as-reduced powder.

4. Conclusions

This study proposed a new method to prepare the superconducting compound Nb_3Sn. It was directly synthesized by reducing the mixture of the oxides or the hydroxides containing niobium and tin atoms with a Sn/Nb ratio of 1/3. This method consists of the following three steps: (i) preparing the mixed oxides of Nb_2O_5 and SnO_2 by the rapid solidification from the melts, or preparing the amorphous hydroxides by the simultaneous precipitation from the aqueous solution, (ii) reducing them by calcium or magnesium vapour at 973 to 1373 K and directly synthesizng the compound during the reduction, and (iii) annealing the reduced powders to improve the superconducting properties.

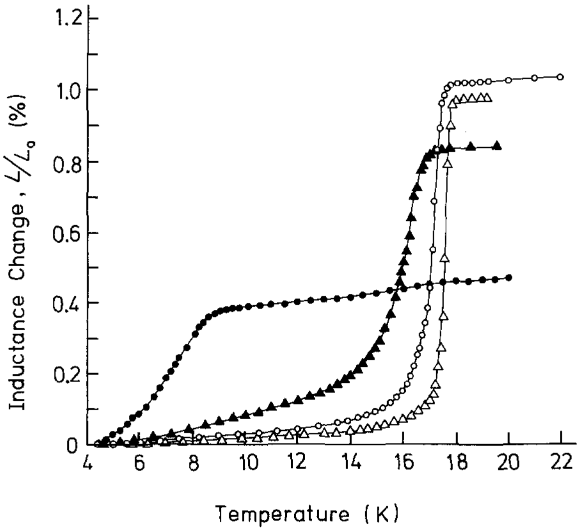


Figure 6 Inductance–temperature curves for the isothermally annealed Nb_3Sn powders at 1273 K for various periods, where the specimens had been reduced by magnesium at 1173 K for 259 × 10^3 sec prior to the annealing. The inductance changes were normalized by that at 4.2 K. (●) As-reduced, T_c = 9.1 K, (▲) 1.8 × 10^3 sec, T_c = 17.0 K, (○) 3.6 × 10^3 sec, T_c = 17.7 K, (△) 86.4 × 10^3 sec, T_c = 18.0 K.

The Nb_3Sn single phase could not be synthesized by the reduction using calcium vapour. It could be obtained by the reduction by magnesium vapour, probably with the aid of a liquid Sn–Mg alloy. By subsequent heat treatment we could obtain the Nb_3Sn single phase with an A15 type crystal structure, whose critical temperature of superconducting transition agreed well with the reported value, 18.0 K.

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