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The Preparation of Niobium Stannide by the Iodide Process

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Nb_3Sn has been prepared by various methods[1,2] because of its good characteristics as a superconductor. This paper will describe the applicability of the iodide process, one of the chemical transport reactions, to the preparation of Nb_3Sn.

Experimental

A Sintered Source Material. About 10 g of a blend of a stoichiometric mixture of Nb and Sn powder*1 was divided into 10 parts; pellets (6 mmϕ × 8 mm) were then made under a pressure of 3×10^3 kg/cm^2. These pellets were sintered at 1000°C for 10 hr in a flow of Ar gas at a flow rate of 2 *l*/min.

The Iodide Process. To carry out the closed-tube transport experiment, fused silica tube (0.8 cm in int. diam., 0.015 cm in wall thickness, and 20 cm in length) containing the source material and a known amount of the transport agent, iodine,*2 was sealed off after evacuating and out-gassing treatment.

This reaction tube was placed in a horizontal tube furnace, which was so designed that the reaction region (5 cm) of this closed system could be uniformly heated at 900°C, and the deposition region (5 cm), at 1000°C. The transport region (10 cm) between the reaction and deposition regions had a linear temperature gradient.

We obtained a thin layer of Nb_3Sn deposited on the silica tube wall at a rate of 0.3 mg/hr.

The chemical compositions of the Nb_3Sn was determined by X-ray fluorescence spectrometric and chemical analytic methods.[1] In the chemical method, the niobium was determined as niobium pentoxide, Nb_2O_5; after volatilizing the tin as its bromide, the tin was determined iodometrically. In the X-ray spectrometric method, a ratio method was employed in which the net intensities of the X-ray spectral lines of niobium and tin were measured and their ratio calculated. The purity of Nb_3Sn was 70.0±0.2 wt% Nb, 29.6±0.3 wt% Sn (Calcd, Nb, 70.13 wt% Sn, 29.87 wt%).

The X-ray powder diffraction pattern yielded a lattice constant of 5.3 Å for vapor-deposited niobium stannide with a β-tungsten structure.

Results and Discussion

(1) Effects of the Stoichiometry of the Sintered Source Material. The weight ratio of Nb to Sn in the source materials influences the stoichiometry of the deposits. The composition of deposits as a function of the weight ratio of Nb to Sn in the materials is shown in Fig. 1. As a general tendency, the ratio of Nb to Sn in deposits increases with an increase in this ratio in the materials.

These results may be attributed to the fact that the free-energy changes of Nb and Sn iodides are different; also, Nb and Sn show different reactivities for I_2 molecules because of their differences in intermolecular forces between the gaseous iodine molecules and each atom of the material.*3

The dispersion of data results from the following

1) R. S. Holmes, *RCA Rev.*, **25** (1964).

2) T. L. Chu and J. R. Gavaler, *J. Electrochem. Soc.*, **113**, 1289 (1966). Von H. J. Bode, R. G. Maier and G. Wilhelm, *Z. Naturforsch.*, **19a**, 804 (1964).

*1 Nb and Sn powder were obtained from Mitsuwa Pure Chemicals, Ltd., and Wako Pure Chemicals, Ltd., respectively, and their purity were 99.5% as given by producer.

*2 The iodine was vacuum distilled from the capsule into the reaction tube.

*3 T. Kawai (to be published).

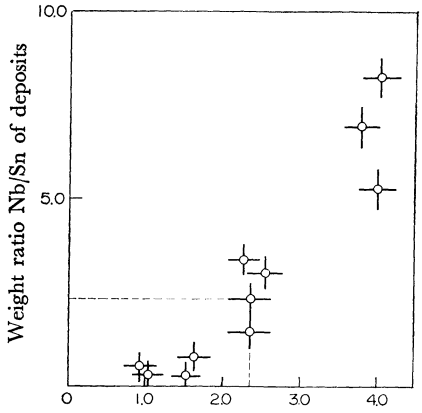

Fig. 1. Effects of the stoichiometry of the sintered source material.

reasons: 1) a small amount of Sn on the surface of these pellets evaporated for sintering because of its volatility, and 2) the mixture was not blended uniformly.

This problem should be resolved by pulverizing these sintered pellets again and using this powder as a source material. However, it is evident that, to obtain a stoichiometric Nb_3Sn, it is necessary to maintain a Nb/Sn ratio of approximately 2.4 in the source materials.

(2) Effects of the Initial Amount of a Transport Agent.[3] The dependence of the transport rate upon the initial amount of the agent, I_2, is depicted in Fig. 2.

In the small-amount range of I_2, the transport rate is approximately proportional to the square root of the concentration.*3 In this range, it may be supposed that the heterogeneous chemical reaction in the reaction region is the rate-determining step.

Above 1.5×10^{-5} mol/cm^3, the transport rate is very litttle dependent on the amount of I_2, because the diffusion rate of gaseous iodides determines the total kinetic rate of the iodide process. We are, therefore, able to obtain the glossy Nb_3Sn deposited on a silica tube wall in this range.

Above 5×10^{-5} mol/cm^3, the natural convection of gaseous iodides may be attributed to the transport rate, and the quantity deposited increases rapidly, but the deposit is a powder and does not have uniform properties.

(3) Other Important Problems. When we apply the iodide process or, in general, the chemical transport reaction to the deposition of the Nb_3Sn film on various substrates, there are other important problems besides the two effects pointed out previously.

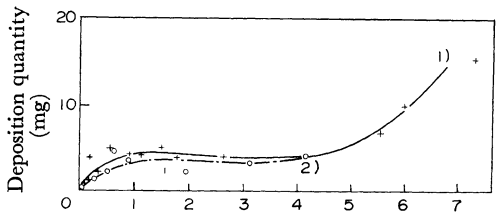

Fig. 2. Effects of the initial amount of a transport agent.

	the temp. of the react. region. °K	the temp. of the deposit. region. °K	a transport length. cm
1) (+)	1173	1273	10
2) (○)	1173	1223	7

The preparing conditions of the pellets.

	pressure kg/cm^2	sintering times hr	sintering temp. °C
1)	$1—3\times10^3$	9—10	1000
2)	3×10^3	10	1000

We must understand how to choose the temperature in the reaction and in the deposition region. In this experiment, we have fixed the temperatures of the reaction and the deposition region at 900 and 1000°C respectively, basing these values on the thermodynamic analysis of Zr and V iodides and on the results of the spoon-gauge experiment.*4

If we had the thermodynamic data of Nb iodides, we could solve the above problems, but these data have not yet been obtained.

In an attempt to solve these problems, we should have further information in addition to the thermodynamic data of Nb iodides, that is, information 1) the chemical form of iodides which contribute to the transport of Nb_3Sn; 2) the heterogeneous reaction rate between gaseous iodines and Nb-Sn surface atoms, and 3) the thermal decomposition rate of gaseous iodides or the deposition rate of Nb_3Sn from the vapor phase.

As to the first point, we have done investigations with the spoon-gauge and the DTA instrument.*5 From this information and from the data of the NbI_5-Nb phase diagram reported by Seabaugh and Corbett,[4] it follows that NbI_3 and NbI_4 contribute more to the transport than does Nb_3I_8. For Sn, it can be deduced from the thermodynamic analysis that SnI_2 is more favorable than SnI_4.

3) T. Hashino and T. Kawai, *Trans. Faraday Soc.*, **63**, 3088 (1967).

*4 T. Kawai and S. Iwata (to be published). The spoon-gauge has been made by Nishiyama Seisakusho Ltd, Osaka, and has the sensitivity of 0.1 mmHg as a result of the improvement of a spoon-form.

*5 A length of 3 cm fused-silica tube containing samples was sealed off and used as a DTA sample container. T. Kawai and S. Iwata (to be published).

4) P. W. Seabaugh and J. D. Corbett, *Inorg. Chem.*, **4**, 176 (1965).

As for the second and third points, we are going to investigate them experimentally and theoretically.

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