JOURNAL OF MATERIALS SCIENCE 5 (1970) 580-603

Experimental Work on the Niobium-Tin Constitution Diagram and Related Studies

J. P. CHARLESWORTH, I. MACPHAIL, P. E. MADSEN
Solid State Division, AERE, Harwell, Didcot, Berks

Three intermetallic phases Nb_3Sn, Nb_6Sn_5 and $NbSn_2$ are formed in the niobium-tin system. Nb_6Sn_5 and $NbSn_2$ appear to be stoichiometric with narrow homogeneity range, but Nb_3Sn can exist over a wide composition range from about 73 to 83 at. % niobium although the niobium-rich compositions are not formed on annealing below 1400° C. Nb_6Sn_5 and $NbSn_2$ form peritectically at 930 and 845° C respectively. The three phases appear to be stable to low temperatures, but Nb_3Sn and Nb_6Sn_5 are slow to form below about 800° C. The solubility of niobium in liquid tin is small at temperatures below 1000° C and the solid solubility of tin in niobium decreases from about 9 at. % tin at the peritectic temperature of Nb_3Sn to about 1 at. % tin at 1495° C and is negligible below 1000° C. An equilibrium diagram is constructed from the present data and from other published information.

1. Introduction

Since the discovery by Kunzler, Buehler, Hsu, and Wernick [1] that the compound Nb_3Sn will carry large superconducting currents in very high magnetic fields, a great deal of research on the properties and occurrence of this phase has been carried out. Several papers on the niobium-tin equilibrium diagram have been published. These have been reviewed by one of the authors [2] together with relevant information on the diagram in other publications on the preparation or properties of Nb_3Sn.

The present work on the niobium-tin system arose from the need to understand the complicated multiphase structures of niobium-tin superconductors at a time when the only published diagram [3] suggested that Nb_3Sn was the only intermetallic compound formed in the system. A preliminary report [4], differing in interpretation in some respects, was read to the Institute of Metals Symposium on High Field Superconductors in 1964, but no proceedings of this symposium were published.

2. Experimental Methods

2.1. Materials

Specpure tin and 99.8 to 99.9% niobium rods were used to prepare the diffusion specimens and some melted alloys. Niobium bar I was used for these melted alloys and most of the diffusion specimens. Its analysis (table I) indicates that the principal impurities were 500 ppm oxygen, 230 ppm nitrogen, 200 ppm iron and 90 ppm carbon.

Fine (~ 150 mesh) niobium powder was used for preparing compacts and some cast alloys. The analysis (table I) shows the material to be rich in tantalum (1500 ppm) and to have high iron, silicon and molybdenum contents (300 ppm each). The hydrogen and nitrogen contents were similar to the rods, but the oxygen content was much higher (4000 ppm). A high oxygen content seems unavoidable in fine powder niobium; samples obtained from two other sources had oxygen contents of 2700 and 5000 ppm.

The chemically pure tin used in preparing compacts had a high oxygen content (1800 ppm), the other principal impurities being indium 150 ppm, hydrogen 75 ppm, nitrogen 60 ppm, lead 50 ppm and iron 30 ppm (see table I).

2.2. Specimen Preparation

2.2.1. Melting and Casting

Rapid induction melting under argon at pressures slightly above atmospheric was employed in preference to arc casting which invariably produced badly segregated ingots. Rf heating (440 kcs) was unsatisfactory since homogeneous alloys could not be produced from mixtures of niobium and tin lumps or from pressed

TABLE I Impurity content (in ppm) of starting materials

Impurity element	Niobium bars								Niobium powder	Chemically pure tin powder
	Bar 1	Extreme values other bars		Interstitial content of another bar	Bar 2	Bar 3	Bar 4	Bar 5		
		upper	lower							
Al	< 30	50	30		< 50	< 50	< 50	< 50	< 30	5
Bi										7
Cd										1
Co	< 10	< 15	< 2		< 15	< 15	< 15	< 15	< 10	< 5
Cr		150	< 15		100	70	150	< 15		1
Cu		< 15			< 15	< 15	< 15	< 15		2
Fe	200	450	< 20		150	70	150	< 20	300	30
Ge										< 2
In										150
Mg		50	< 15		< 15	< 15	< 15	< 15		7
Mn	< 15	< 15	< 2		5	< 2	< 2	< 2	< 15	< 2
Mo	< 10	100	< 15		< 15	70	70	< 15	300	< 5
Ni	< 5	30	< 5		15	15	30	< 5	5	< 5
Pb		< 3	< 2		< 3	< 3	< 3	< 3		50
Sc	< 70								< 70	
Si	< 70	300	70		300	300	150	70	300	
Sn		300	< 2		< 2	300	200	< 2		remainder
Ta	<400	2900	<100		800	2400	1400	100	1500	
Ti	< 30	300	< 15		< 15	150	70	< 15	30	< 5
V	< 15	900	< 15		< 15	150	700	< 15	20	< 5
Zn										5
Zr	<100									
W									< 100	
C	90			135						
H	55			21					80	75
N	230			95					230	60
O	500			500					4000	1800

powder compacts containing more than 60 at.% tin. Using hf heating (5 kcs) fairly uniform alloys of all compositions could be obtained even if the starting materials were fairly massive lumps of niobium and tin. Both beryllia and zironcia appeared to be suitable crucible materials, but zirconia was generally employed because of its high melting point and absence of health hazards. These cast alloys always contained dark particles, arranged in dendritic fashion, which remained even after annealing at 1600° C.

2.2.2. Diffusion Samples

The layers formed between solid niobium and liquid tin were studied to provide information on the phases formed and the rates of diffusion.

In most cases the tin was contained in a 2 in. long thick-walled 0.28 in. diameter niobium can closed by an electron beam-welded end cap. The niobium surface was in the machined condition, the cans being cleaned in carbon tetrachloride and methylated spirits before being half-filled with a similarly cleaned, machined rod of spec-pure tin. A few experiments were done with sheet samples dipped into a tin-filled alumina crucible.

2.2.3. Compacts

Difficulty was experienced in the metallographic preparation of pressed powder compacts which were porous and friable even after heat-treatment. However, during a study of the fabrication of wires by the Kunzler technique [1], which involves the swaging or drawing of niobium-tin compacts in a niobium sheath, it was found that metallographic preparation became very much easier after a small amount of deformation. Hence compacts prepared in this fashion and given about 50% reduction in area were used to study phases formed on annealing. This type of specimen had the advantage that the niobium sheath provided a reference for identifying the phases when the anodising technique was employed. Tin losses from these specimens, although smaller than from unsheathed specimens, were sufficient to produce a thin layer of niobium-tin phases on the outside of the niobium sheath on annealing.

2.3. Heat-Treatment

The compacts and induction-melted samples, wrapped in niobium foil and placed in a degassed alumina crucible, were annealed in silica tubes under a reduced argon atmosphere. This technique could be used up to 1200° C for long times, or up to 1400° C for times of a day or so. It is likely that contamination by oxygen or nitrogen diffusing through the silica capsule occurred in specimens annealed above about 1200° C since there was a marked hardening of the niobium sheath for specimens annealed at 1400° C, Vickers hardnesses of 363 and 380 being obtained after this treatment, compared with values of between 113 and 149 after annealing at 700 to 1200° C.

Some annealings at temperatures up to 1800° C were carried out in a molybdenum-wound furnace with the windings protected by a hydrogen atmosphere.

The diffusion can samples were generally sealed in silica capsules and annealed in a horizontal furnace followed by air-cooling or water-quenching, but a few were heated in an evacuated vertical tube furnace and oil-quenched. The strip samples were annealed inside evacuated silica capsules in a vertical furnace and quenched.

2.4. Metallography

Apart from the difficulties with porous compacts mentioned previously, the main problems in metallographic polishing were due to the marked tendency to form a flowed surface layer during mechanical polishing of niobium and to the fact that the large difference in hardness between the soft tin and the extremely hard intermetallic compounds formed adjacent to it led to the production of a marked step during polishing. The technique developed to overcome these problems is described with later improvements by Macphail [5].

Cathodic ion-bombardment etching [6] was used in preference to chemical etching as many of the specimens were very porous. The different phases etched at different rates so that their occurrence, distribution and grain size could be observed. The very slight colour differences, combined with different behaviour under polarised light, allowed the phases to be identified in many cases, but easier and less ambiguous identification was possible using an anodising technique. A solution originally developed by Picklesimer [7] for zirconium alloys has generally been adopted (e.g. [8, 9]) to distinguish the intermetallic phases in niobium-tin specimens. The present authors having obtained variable results with this solution, experimented with simpler solutions and found that a 10% citric acid solution gave satisfactory results in all specimens containing little or no free tin. Where free tin was present similar anodised colours could be obtained by adjusting the voltage to produce the correct colour on some phase, usually pure niobium, which had been identified by some other means. The anodising technique using 10% citric acid is described in detail by Macphail [10].

Using either anodising solution, the grain structure within the phases could sometimes be observed due to a slight expitaxial effect in the anodised layer but these small colour differences within phases only rarely caused any difficulty in distinguishing between phases.

2.5. Electron Probe Microanalysis

Electron probe microanalysis was performed using a CAMECA machine, the intensities of the Nb L α and Sn L α radiations from the sample being compared with those from pure niobium and tin standards and the ratios corrected for absorption and atomic number effects by the procedure of Thomas [11] and Shaw [12]. The compositions of the compounds were established initially using unanodised specimens (table IIA) but, since it was sometimes difficult to distinguish between phases in this condition, the specimens were later analysed in the anodised condition (table IIB). As the anodised specimens were in non-conducting mounts a layer of carbon was deposited by evaporation to prevent build-up of charge on the specimens during the analysis.

While the totals of niobium and tin content for the unanodised specimens were 100 ± 1 wt %, the totals for the anodised specimens were only 95 to 97 wt % even when anodised carbon-coated standards were used. The results for these specimens have therefore been adjusted by increasing the niobium and tin contents in proportion to their weight percentages to bring the total to 100%. The omission of this procedure would decrease the average niobium and tin contents of Nb_3Sn by 2.2 and 0.9 at. % and those of $NbSn_2$ by 0.5 and 1.3 at. % respectively.

There is also other evidence that anodic layers may cause errors in analysis, especially on pure niobium. The authors have found apparent tin concentrations of 5 at. % in anodised specimens in regions which showed no tin when the anodic layer was removed.

TABLE II Compositions of various phases determined by electron microprobe analysis (compositions in atomic percentages)

Type of specimen	Annealing time	temp.	Feature of interest	α–Nb Nb	Sn	Nb_3Sn Nb	Sn	Nb_6Sn_5 Nb	Sn	$NbSn_2$ Nb	Sn	Tin Nb	Sn
A Unanodised specimens													
Diffusion can	350 h	900° C	layer			73.9	26.5						
			crystal			72.6	28.2						
	1 week	870° C	layer					53.6	46.4				
			crystal					54.1	44.9				
			crystal					53.8	45.2				
		700° C	layer							32			
Sintered compact	1 day	1400° C				73.6	26.3					n.d.	100
	1 day	1000° C				74.3	26.3(1)						
	1 week	900° C		100	n.d.	73.4	25.1	53.1	45.7				
	1 week	850° C		100	n.d.			54.3	45.2(2)	31.5	64.7(2)		
	1 week	700° C		100	n.d.					34.0	66.0		
B Anodised specimens													
Diffusion can	7 days	1390° C				75.9	24.1						
	6 days	1000° C	layer			73.8	26.2						
			crystal			74.3	25.7						
Sintered compact	1 day	1400° C				75.1	24.9						
	1 day	950° C		100	n.d.	74.0	26.0						
	1 week	925° C		100		74.8	25.2						
	6 weeks	650° C				73.3	26.7	54.2	45.8	33.5	66.5		
Cast alloys	1 week	600° C	concentration variation in Nb_3Sn			76.7 to 73.1							
	3 days	825° C	average concentration			76.5(3)							
			concentration at grain centre			80.0(3)	20.0						
	as cast		composition at centres of 3 grains		7.2 5.6 8.8								
	1 day	1600° C	mean value	96.3	3.7	86.5	13.5						
			"most likely" value	97.2	2.2	82.0	18.8						
	1 day	1495° C	mean value	98.9	1.1	83.9	16.1						
			"most likely" value	98.9	1.1	82.9	17.1						
	5 weeks then 1 week	870° C 830° C				74.4	25.6	52.8	47.2	31.7	68.3		
	1 day	830° C				75.3	24.7			31.0	69.0	n.d.	
	2 weeks	825° C				76.5	23.5			31.8	68.2		
	2 weeks then 3 days	825° C 830° C				76.8	23.2			31.8	68.2		
	3 days	820° C				76.0	24.0			32.0	68.0	0.13	
	8 weeks	775° C				77.1	22.9			32.8	67.2		
	10 days	650° C				75.9	24.1			31.4	68.6		

n.d. not detected.

(1) Variation in the composition – extreme values 75.8 at. % Nb – 25.6 at. % Sn to 72.8 at. % Nb – 27.1 at. % Sn.

(2) Beam drifting, values probably not very reliable.

(3) Values determined on different occasions.

2.6. X-ray Methods

Specimens from ground-sintered compacts or from crushed crystals extracted from diffusion specimens were examined using Cu Kα radiation in a Philips powder camera or a Guinier camera. Since some of the patterns from crushed crystals could not be identified from early published structures for the niobium-tin intermetallic phases, single crystal structure determinations were undertaken on crystals formed in the tin-rich liquid of diffusion specimens. These crystals were examined in a Weissenberg camera using Cu Kα radiation.

2.7. Superconductivity Measurements

Details of the inductive method of transition temperature measurement, together with the results obtained, have been published by Charlesworth [13]. Care was taken to avoid the shielding of the phases of interest by multiply-connected regions of higher transition temperature phases, a phenomenon which is believed to have led to

TABLE III Summary of metallographic observations on niobium can diffusion specimens

Temp. (° C)	Time of annealing (in days)	Type of cooling	Phases present in diffusion zone				Thickness of layers (in mm) of diffusion zone			Metallographic observation of diffusion zone and crystals in melt
			Nb_3Sn	Nb_6Sn_5	$NbSn_2$	buff phase	Nb_3Sn	Nb_6Sn_5	$NbSn_2$	
500° C	15	WQ	—	—	√	—	—	—	—	$NbSn_2$ present in isolated patches and not as uniform layer
600° C	10	WQ	—	—	√	√	—	—	0.023	fairly regular layer, buff phases intermingled with $NbSn_2$
600° C	42	WQ	—	—	√	√	—	—	0.049	fairly regular layer, large $NbSn_2$ crystals in the tin
700° C	10	WQ	—	—	√	√	—	—	0.009	large $NbSn_2$ crystals grew from $NbSn_2$ into tin
700° C	30	WQ	—	—	√	√	—	—	0.100	fairly regular layer, intermingled with buff phase which was reduced in quantity on repolishing specimen
770° C	21	WQ	—	—	√	√	—	—	0.132	some buff phase present at $NbSn_2$ grain-boundaries
800° C	16	WQ	√	√	√	—	0.001	0.008	0.030	
810° C	9		—	—	√	—	—	—	0.078	buff phase present at $NbSn_2$ grain-boundaries
810° C	10	WQ	—	—	√	—	—	—	0.090	fairly regular layer, crystals of $NbSn_2$ in tin
	10	WQ	—	—	√	—	—	—	0.094	layer fairly regular but contains cracks, another phase possibly present but examination hampered by staining adjacent to the cracks
830° C	2	WQ	?	√	√	—	0.001 ?		0.038	fairly regular layers
	2	WQ	√	√	√	—		0.0015	0.042	rather irregular layers
	7	WQ	—	√	√	—	—	0.053		fairly regular layer containing some $NbSn_2$ (possibly precipitated on cooling) with the Nb_6Sn_5
	7	WQ	√	√	—	—		0.065	--	fragmentary traces of Nb_3Sn at Nb_6Sn_5 – Nb interface
	21	WQ	√	√	√	possibly present	0.002	0.002	0.186	
850° C	7	WQ	—	√	—	—	—	0.120	—	fairly regular layer, Nb_6Sn_5 and $NbSn_2$ crystals present in tin
	7	WQ	—	√	—	—	—	0.035	—	
870° C	7	WQ	—	√	√	—	—	0.070		fairly regular layers, Nb_6Sn_5 crystals in tin
	21	WQ	√	√	—	—	0.003	0.068	—	fairly regular layers, Nb_6Sn_5 crystals in tin
885° C	7	WQ	√	√	—	—	0.002	0.049	—	rather irregular layers, Nb_6Sn_5 crystals in the tin
	7	WQ	?	√	—	—		0.021–0.030	—	
890° C	7	WQ	√	√	—	—	0.010	0.015	—	very irregular layers
900° C	7	WQ	√	—	—	—	0.306	—	—	rather irregular layers, Nb_6Sn_5 crystals in the melt
	7	WQ	√	—	—	—	0.340	—	—	
	21	WQ	√	√	—	—	0.035	0.030	—	
945° C	7	WQ	√	—	—	—	0.068	—	—	very variable thickness of layer
	7	WQ	√	—	—	—	0.055	—	—	
	21	WQ	√	—	—	—	0.160	—	—	fairly regular layer; many very fine particles of Nb_6Sn_5 at the Nb_3Sn – Sn interface
1000° C	6	AC	√	√	—	—	0.036		—	very thin layer of Nb_6Sn_5 at the Nb_3Sn – Sn interface; Nb_6Sn_5 crystals in tin

TABLE III continued

Temp. (° C)	Time of annealing (in days)	Type of cooling	Phases present in diffusion zone				Thickness of layers (in mm) of diffusion zone			Metallographic observation of diffusion zone and crystals in melt
			Nb_3Sn	Nb_6Sn_5	$NbSn_2$	buff phase	Nb_3Sn	Nb_6Sn_5	$NbSn_2$	
1010° C	6	AC	√	√	—	—	0.034		—	thin layer of Nb_6Sn_5 (produced on cooling?) at $Nb_3Sn - Sn$ interface; crystals of Nb_6Sn_5 and possibly $NbSn_2$ in the tin
1060° C	3	AC	√	—	—	—	0.027	—	—	layers of $NbSn_2$ formed around Nb_6Sn_5 crystals in tin
1290° C	3	AC	√	—	—	—	0.020	—	—	very irregular layer of Nb_3Sn formed with thin layer of Nb_6Sn_5 at the $Nb_3Sn - Sn$ interface (probably produced on cooling); crystals of Nb_6Sn_5 and $NbSn_2$ in the tin; possibly another phase (oxide or nitride?) between Nb_3Sn and Nb in places
1390° C	7	AC	√	√	—	—	0.070		—	very irregular layer of Nb_3Sn formed with thin Nb_6Sn_5 layer (produced on cooling?) at the $Nb_3Sn - Sn$ interface; crystals of Nb_6Sn_5 and $NbSn_2$ in the tin

Bracketed results indicate different microspecimens taken from the same can.
WQ water-quenched.
AC air-cooled.

errors in some published work.

2.8. Thermal Analysis

Initially the thermal analysis apparatus described in reference [14] was employed but after the thermocouple was isolated from the vacuum system to prevent contamination by tin vapour the thermal arrests recorded were too broad to obtain useful data. Another furnace unit was consequently adopted with the thermocouple contained in an alumina tube which entered the vacuum system through a Wilson seal. The arrests obtained were reasonably sharp and fairly reproducible on samples of the same composition.

3. Experimental Results on Diffusion Samples

Sealed niobium cans half-filled with tin were annealed for periods of 2 to 42 days at temperatures between 500 and 1390° C. The metallographic observations on these specimens are summarised in table III which shows the presence and average thickness of layers of the various phases in the diffusion zone with brief descriptions of the regularity of the diffusion layers and of the crystals found in the tin.

3.1. Phase Identification

Layers of intermetallic phases were observed to have formed between the niobium and tin, and at some temperatures three layers were clearly visible. Anodising stained the layers (in order of increasing tin content) purple, dark and light brown respectively. The two brown layers responded to polarised light in both unanodised and anodised condition.

Microprobe analysis of layers of these three phases showed them to contain 73.9, 53.6 and 32 at. % niobium (see table IIA). These compositions are close to 75, 54.55 and 33.33 at. % niobium which are the compositions for stoichiometric Nb_3Sn, Nb_6Sn_5 and $NbSn_2$ and this nomenclature will be used to describe the three phases although it is realised that some of them may have a wide range of composition.

A fourth colour, a slightly lighter brown than the $NbSn_2$ and henceforth described as the buff-coloured phase, was also observed. This sometimes occurred as arms extending into the diffused layers, but more generally adjacent to the outermost layer in the tin, or around crystals in the melt, as if it had precipitated from the tin on cooling. The distribution of this phase could be greatly altered by repolishing the specimen, whereas the general structure of the layers was not greatly affected. Microprobe measurements showed the buff phase to be slightly richer in tin than the $NbSn_2$ phase but it is doubtful whether this difference is really significant, as the areas examined were small and the electron beam probably straddled the tin matrix, hence increasing the apparent tin content. The structure of this phase and its content of other elements, e.g. oxygen, were not determined.

3.2. Effect of Temperature of Annealing

The diffusion layers of the three phases showed a columnar microstructure under all conditions of formation studied.

$NbSn_2$ was the only phase, apart from the buff-coloured phase, found in the diffusion layer of specimens annealed below $\sim$ 800° C and was also the thickest layer in specimens annealed up to 830° C. Above this temperature the $NbSn_2$ layer was absent apart from traces of $NbSn_2$ in a specimen annealed for 1 week at 870° C where it is thought the $NbSn_2$ may have formed on cooling.

Nb_3Sn was the thickest layer in specimens annealed at 900 to 1390° C and it was generally observed in specimens annealed at temperatures down to 800° C. The layer formed after 16 days at 800° C was only 1 μm thick and it was concluded that a layer of Nb_3Sn was probably present at lower temperatures but was too thin to be observed in the optical microscope without special sectioning techniques.

Nb_6Sn_5 was observed in specimens annealed between 800 and 900° C, being the thickest layer between 850 and 890° C. Below 800° C the absence of Nb_6Sn_5 could be due to slow diffusion rates rather than to the instability of the compound. A thin layer of Nb_6Sn_5 found in specimens air-cooled from 1000, 1010, 1290 and 1390° C was thought to have formed on cooling. In specimens water-quenched from 945° C no Nb_6Sn_5 layer was observed, though very fine Nb_6Sn_5 crystals were found at the Nb_3Sn-tin interface in one case.

The microstructure of the diffusion zones varied from fairly uniform layers, occasionally broken up by intrusions of tin or the buff phase, to layers of very variable thickness having a deeply serrated outline. The irregularity of the layer generally increased with the annealing temperature, but this was not the only factor involved since both regular and irregular interfaces were observed from different microspecimens taken from the same can. For a given specimen the thickness was reasonably constant from section to section but the results could vary considerably on different specimens given the same heat-treatment.

The thickness of the diffusion layer of Nb_3Sn did not increase significantly with temperature. For example, after 3 days at 1290° C the layer thickness was 20 μm compared with 27 μm obtained after 3 days at 1060° C. From this and from the jagged outline of the diffusion layers it seemed likely that erosion of the layer was taking place.

3.3. Effect of Time of Annealing

It had been planned to follow the growth of the diffusion layers with increasing time but the marked discrepancies found between, for example, 35 μm thickness of Nb_3Sn after 3 weeks at 900° C and $\sim$ 320 μm after only 1 week at 900° C indicated that reproducible growth data would not be obtained. A few experiments (described in sections 3.4 and 3.5 below) showed that the purity of or degree of cold-work in niobium were not the prime causes of this erratic growth. It seemed more probable that destruction of the diffusion layers by erosion or solution was occurring. Since no further useful constitutional data could be obtained these experiments were not pursued. An understanding of the reaction of niobium with tin is clearly of great importance as far as the production of Nb_3Sn superconductors by diffusion reactions is concerned and has formed the subject of a separate study by Old and Macphail [15].

3.4. Effect of Niobium Purity

Most of the diffusion cans had been made from niobium rod I but a few had been machined from other rods of the same stock and it was unfortunately impossible to trace the cans back to a particular bar. When variability in the diffusion results was encountered some of the bars were analysed and it was found that some of the elements showed quite a large variation from bar to bar with extreme values (table I) for iron from $<$ 20 to 450 ppm, silicon 70 to 300 ppm, titanium $<$ 15 to 300 ppm and vanadium $<$ 15 to 900 ppm. The greatest variation, from $<$ 100 to 2700 ppm, was observed in the tantalum content. The interstitial impurity content of another bar was analysed but this was not greatly different from bar I.

Strip samples from four bars (nos 2 to 5) covering the whole range of tantalum contents, and including one with a high vanadium content, were prepared metallographically as far as 600 grade silicon carbide papers, immersed in tin and annealed for 1 week at 850° C. The diffusion product on all four specimens consisted of a layer of Nb_3Sn about 5 μm thick adjacent to the niobium and a $NbSn_2$ layer adjacent to the tin which penetrated into the main Nb_6Sn_5 layer as deep inlets. The total layer thickness varied a little from side to side of the specimen, but all the values lay in the region from about 12 to 30 μm except for one side of the specimen from bar 5, the purest material, where a layer about 600 μm thick containing much free tin was observed. Hence any small composition effects at this temperature can be completely swamped by different growth conditions on opposite faces of a specimen.

3.5. Effect of Cold-Work

Variation in the amount of cold-work introduced during machining is another possible cause of the erratic growth of the diffusion layers since experiments on swaged compacts, described in section 4, indicate that cold-work may assist the formation of Nb_3Sn at lower temperatures.

One diffusion can specimen, flattened by rolling and annealed for a week at 850° C, produced fairly regular diffusion zones consisting of a thin layer about 5 μm thick of Nb_3Sn adjacent to the niobium, a layer of Nb_6Sn_5 about 15 to 25 μm thick and a 10 to 20 μm thick $NbSn_2$ layer adjacent to the tin. For comparison an undeformed can annealed at this temperature gave a diffusion zone of variable thickness of 35 to 120 μm in which only Nb_6Sn_5 was identified. Thus cold-work apparently altered the phases formed, perhaps by assisting nucleation, and produced a more regular growth of the layers. The regular growth may however have been the result of restricting the thickness of the tin and reducing the convection currents (see Old and Macphail [15]).

Strip samples of niobium which had been annealed and deformed 90% by rolling were prepared metallographically as far as 600 grade silicon carbide papers and annealed in tin for 1 week at 850° C. The diffusion layers contained the three intermetallic compounds – Nb_3Sn adjacent to the niobium, Nb_6Sn_5 forming the greater part of the zone but mixed in places with $NbSn_2$ and a 5 μm layer of $NbSn_2$ adjacent to the tin. In contrast to the experiments on cans the sheet samples gave Nb_3Sn layers which were barely visible on the worked samples compared with a 5 μm layer on annealed samples. In worked samples the diffusion zones were of fairly uniform thickness with only slight variation on opposite faces (about 30 and 37 μm in one sample and 22 and 25 μm in another) but a greater variability was observed with annealed samples (about 35 and 45 μm in one sample, and about 15 and 102 μm in another). It appears that although variation in the degree of cold-work in the niobium may affect the uniformity of layer growth it cannot account for the variability encountered in the diffusion results.

3.6. Crystals in the Tin

Crystals of the various phases were present in the tin, some having been nucleated at, or very close to, the diffusion layers, while others had formed in the centre of the tin well away from the walls of the container. Specimens air-cooled from high temperatures, where the diffusion zone was predominantly Nb_3Sn, contained mainly Nb_6Sn_5 or $NbSn_2$ crystals, indicating a decrease in the solubility of niobium in liquid tin on cooling which was confirmed by formation of $NbSn_2$ layers around Nb_6Sn_5 crystals in some experiments. In specimens water-quenched from temperatures below about 1000° C the crystals appeared from microexamination of anodised microspecimens to have the same composition as the main component of the diffusion zone and electron probe microanalysis showed that large Nb_3Sn crystals grown at 1000° C and 900° C, and Nb_6Sn_5 crystals grown at 870° C had the same composition within 1.3 at. % as the corresponding diffusion layer (table II). However, X-ray diffraction patterns and superconducting transition temperature measurements showed that some small crystals of phases forming at low temperatures must also have been present.

Nb_3Sn particles up to 0.065 cm long were extracted from the tin after diffusion runs of 350 h at 900° C or 500 h at 1000° C. The shape of many of these particles suggested that they were single crystals and this was confirmed by X-ray single crystal techniques in the case of one large crystal. It was thought that larger single crystals might be grown by modification of this technique but a few preliminary experiments such as increasing the annealing time, or soaking at a higher temperature and then slowly cooling, did not produce significantly larger crystals and the yield of crystals was extremely variable.

Most of the Nb_6Sn_5 and $NbSn_2$ particles were obviously polycrystalline aggregates and others which appeared from their shape to be single crystals turned out to contain more than one crystal when examined by X-ray single crystal techniques. This was apparent too in the microspecimens where the $NbSn_2$ characteristically grew as elongated bicrystals (generally nucleated from the diffusion zone) with the crystal boundary parallel to the long axis of the bicrystal. Nb_6Sn_5 crystals often appeared in fan-shaped groups in which many crystals seemed to have nucleated from one point. An inclusion was occasionally present at this place, but sometimes quite definite growth twins were observed (fig. 1).

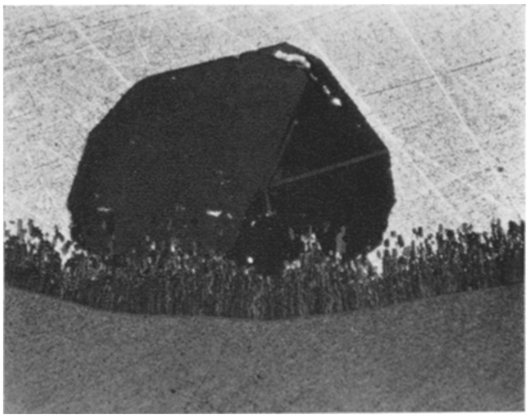

Figure 1 Nb_6Sn_5 particle formed in diffusion specimen annealed 3 weeks at 870° C, showing growth twins. Anodised specimen photographed under polarised light (× 100).

A fine dot-like precipitate observed in the tin was too small to identify by optical techniques. These particles are believed to be $NbSn_2$ [15] since their shape on examination by electron microscopic techniques is similar to larger $NbSn_2$ particles identified by optical metallography.

4. Experiments with Sintered Compacts

Though niobium and tin powders are less pure than the bulk metals, especially with regard to their oxygen content, many annealing experiments were done on compacts since the fine size of particles meant that equilibrium could be more readily achieved. Even so equilibrium was only attained at the higher temperatures and at many temperatures all three intermetallic phases were present as well as unreacted niobium and tin. Thus the temperatures at which these phases formed could be determined but little information could be gathered about their composition range.

The metallographic evidence for the existence of the phases at various temperatures is entered in tables IV and V, a question mark against a phase indicating some doubt as to its existence in the specimen. In the case of Nb_3Sn and Nb_6Sn_5 the doubt arose where very thin layers $\lesssim 1\ \mu m$ were present, generally in specimens annealed at temperatures at the bottom of the range for observation of these phases. Usually, if a suspected layer was traced far enough, areas could be found where the layer was locally thicker and could be identified unambiguously. More doubts arise concerning the presence of $NbSn_2$ at the annealing temperature since this phase can undoubtedly precipitate very rapidly from tin on cooling. Consequently the presence of $NbSn_2$ crystals in tin, or the existence of a very thin $NbSn_2$ layer adjacent to the tin, was not taken as evidence for the stability of $NbSn_2$ at temperature. It was sometimes difficult to distinguish small $NbSn_2$ particles from the impurity phase which anodised to a light yellowish brown colour, or from a grain of Nb_6Sn_5 which, because of its orientation, had a lighter brown anodised colour than the other Nb_6Sn_5 grains. This confusion only occurred with $NbSn_2$ particles too small to be readily identified by their strong response to polarised light.

A general observation on all the compacts was that the intermetallic phases, especially Nb_3Sn, could be detected as forming at lower annealing temperatures in the region adjacent to the niobium sheath than around the niobium particles in the core. The niobium sheath had a lower oxygen content than the niobium particles (table I), but the difference in behaviour may have been due rather to the greater deformation the sheath had undergone since, in the core, the tin will bear the brunt of the deformation until the niobium particles become locked together. This extra deformation might also have ruptured the oxide layer on the sheath, allowing rapid attack by the tin. The difference in behaviour would then be expected to disappear at temperatures where the oxide layer could disperse by dissolving in the niobium.

4.1. Identification of Phases in 50 and 75 at.% Niobium Compacts

The phases present in the system were identified in 50 and 75 at. % niobium compacts which had been annealed from 1 day to 2 months at 400 to 1400° C (table IV). The compacts were examined initially in the cathodically etched condition and subsequently in the anodised condition.

The microstructures of the 50 at. % niobium alloys proved easier to interpret and formed the basis for the identification of three intermetallic phases. After 1 month at 400° C the specimen contained unreacted niobium and tin, with a grey phase which responded strongly to polarised light present in the tin, sometimes in sufficient quantity to join up neighbouring niobium particles. A compact annealed 1 week at 600° C still showed unreacted niobium, but the tin had all reacted to form the grey phase. Two months annealing at 700° C gave a similar structure, but another grey phase, responding to polarised light less strongly than the first, was visible as envelopes round the niobium particles. After 1 week at 800° C these layers had thickened considerably, in places joining neighbouring envelopes to form a path which was practically continuous through the specimen, and a very thin layer of another phase had appeared around the niobium particles. After a month at 850° C the strongly polarising phase had disappeared and the weakly polarising phase now constituted the matrix. The phase forming envelopes round the niobium seemed to show no response to polarised light. These layers had thickened after a week at 900° C but the weakly polarising phase was still present. At 1000° C the non-polarising phase occupied practically all the specimen but some free tin was present. One week's anneal at 1400° C gave a similar structure, except that a much larger grain size was visible.

The compositions of larger particles of the three phases were determined by electron probe microanalysis (table IIA) to be:

non-polarising phase	73.4 to 74.3 at. % Nb
weakly polarising phase	53.1 to 54.3 at. % Nb
strongly polarising phase	31.5 to 34.0 at. % Nb.

These are very similar to the phases Nb_3Sn, Nb_6Sn_5 and $NbSn_2$ identified in diffusion experiments. The non-polarising phase was found from X-ray powder patterns to possess the β-W structure.

TABLE IV Metallographic evidence for the presence of intermetallic phases in sintered compacts

Final annealing temperature	75 at. % niobium		55.5 at. % niobium		50 at. % niobium		34.0 at. % niobium		Miscellaneous alloys		
	treatment	phases present	treatment	phases present	treatment	phases present	treatment	phases present	composition	treatment	phases present
1400° C	1 day	Nb_3Sn									
1200° C	1 day	Nb_3Sn									
1000° C	1 day	Nb_3Sn									
950° C	1 day after 1 day at 800° C	Nb_3Sn			1 week	Nb_3Sn					
935° C			5 days	Nb_3Sn							
930° C							1 day	Nb_3Sn			
925° C			1 day after 1 day at 850° C	Nb_3Sn, Nb_6Sn_5							
900° C	1 day after 1 day at 800° C	Nb_3Sn, Nb_6Sn_5			1 week*	Nb_3Sn, Nb_6Sn_5					
					1 month*	Nb_3Sn, Nb_6Sn_5					
870° C			3 days 1 week	Nb_3Sn, Nb_6Sn_5 Nb_3Sn, Nb_6Sn_5							
850° C	1 day after 1 day at 800° C	Nb_3Sn, Nb_6Sn_5			1 week	Nb_3Sn, Nb_6Sn_5, $NbSn_2$	1 day after 2 weeks at 800° C	Nb_3Sn, Nb_6Sn_5			
					1 month	Nb_3Sn, Nb_6Sn_5, $NbSn_2$?					
					1 month	Nb_3Sn, Nb_6Sn_5					
800° C	1 day	Nb_3Sn, Nb_6Sn_5, $NbSn_2$			1 week	Nb_6Sn_5, $NbSn_2$	3 days	Nb_3Sn, Nb_6Sn_5, $NbSn_2$			
					1 week	Nb_3Sn?, Nb_6Sn_5, $NbSn_2$	1 week	Nb_3Sn, Nb_6Sn_5, $NbSn_2$			
725° C	5 days	Nb_3Sn, Nb_6Sn_5, $NbSn_2$									
700° C					8 weeks	Nb_6Sn_5, $NbSn_2$			83.6 at. % Nb	6 days	Nb_3Sn, Nb_6Sn_5, $NbSn_2$
627° C			9 days after 15 days at 870° C	Nb_3Sn, Nb_6Sn_5, $NbSn_2$?			12 weeks	Nb_3Sn, Nb_6Sn_5, $NbSn_2$			
625° C									35.4 at. % Nb	6 days	$NbSn_2$
600° C					1 week	Nb_6Sn_5?, $NbSn_2$					
550° C							12 weeks after 1 day 870° C	Nb_6Sn_5, $NbSn_2$			
500° C			12 weeks	Nb_6Sn_5, $NbSn_2$			12 weeks	$NbSn_2$			
400° C					1 week	$NbSn_2$					
					1 month	$NbSn_2$					

* Identical results obtained on duplicate microspecimens.

Microprobe analysis showed no solubility of tin in the niobium, or of niobium in the tin, even at 1400° C, but it is possible that the niobium had precipitated from the tin as a tin-rich phase on cooling.

A re-examination of these specimens after the anodising technique had been adopted suggested that a very thin layer of Nb_6Sn_5 had formed around the rim of the niobium sheath in the sample annealed for 1 week at 600° C, and that traces of $NbSn_2$ were present in a specimen annealed for 1 month at 850° C. In a specimen annealed for 1 week at 850° C $NbSn_2$ was quite definitely present.

The 75 at. % niobium alloy was annealed for 1 day at 800, 1000, 1200 and 1400° C. At 1000° C and above these specimens consisted of Nb_3Sn and unreacted niobium, while at 800° C only thin rims of Nb_3Sn round the unreacted niobium were present, the remainder being about two-thirds Nb_6Sn_5 and one-third $NbSn_2$. Pieces of this latter specimen reannealed for 1 day at 850 and 900° C showed only Nb_3Sn and Nb_6Sn_5 among the reacted phases, while after reannealing for 1 day at 950° C only Nb_3Sn and unreacted niobium were present, suggesting that Nb_6Sn_5 and $NbSn_2$ were only stable below 950 and 850° C respectively.

4.2. Annealing of Compacts of Stoichiometric Nb_6Sn_5 and $NbSn_2$ Composition

In an attempt to prepare single-phase samples of Nb_6Sn_5 and $NbSn_2$ by sintering, compacts containing 55.5 and 34.0 at. % niobium were given long heat-treatments to produce single-phase structures. These attempts were unsuccessful as unreacted niobium or tin, or an unwanted intermetallic phase, was always present. The results of these annealing experiments, given in table IV, show that on annealing above 930° C Nb_3Sn alone is formed, Nb_6Sn_5 formed at 870° C is stable at 925° C and both Nb_6Sn_5 and $NbSn_2$ are formed on annealing at 500° C.

4.3. Annealing 35.4, 56.1, 65.7, 74.9 and 83.6 at. % Niobium-Tin Compacts at 240 to 950° C

It was thought that the absence of a phase at some temperatures might be the result of an excess of one of the constituent elements rather than instability of the phase, and that it would be desirable to examine a series of compositions annealed under identical conditions. Consequently sheathed compacts containing 35.4, 56.1, 65.7, 74.9 and 83.6 at. % niobium (30, 50, 60, 70 and 80 wt % niobium respectively) were annealed for 1 week at 925, 860, 850, 825, 775, and 750° C, and for 6 weeks at 650 and 240° C. The phases found are entered in table V. All three phases were found at some compositions on annealing between 650 and 850° C, but only Nb_3Sn and Nb_6Sn_5 formed at 860 and 925° C.

At 240° C a light brown phase presumed to be $NbSn_2$ was present as needles in the tin (fig. 2), in contrast to the microstructure obtained after annealing at higher temperatures where the $NbSn_2$ grew as layers around the niobium or niobium-rich phases. Electron probe microanalysis of the needles suggested a niobium content of 10 to 12 wt % the remainder being tin, but, since the needles were thin and narrow, the tin content would be exaggerated and the needles could have been $NbSn_2$, although the possibility of an interstitial phase was not ruled out. In some areas there was sufficient of this phase to suggest it must have formed at temperature.

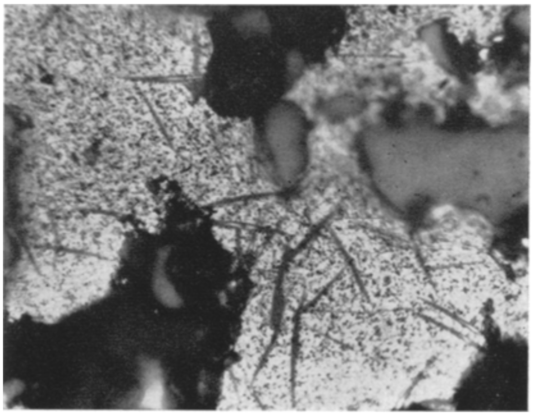

Figure 2 Needle-shaped particles formed in tin of 35.4 at. % niobium-tin compact annealed 6 weeks at 240° C, anodised (× 490).

5. Thermal Analysis Experiments

Thermal analysis curves were obtained from cast samples with 24.2, 35.4, 46.0, 56.1 and 65.6 at. % niobium for temperatures up to 1000° C. In addition to the arrest at the melting point of tin the curves showed arrests during the heating parts of cycles at 833 to 870° C and 922 to 935° C with corresponding arrests on cooling at 810 to 838° C and 870 to 878° C respectively. The temperatures on heating agree approximately with the upper temperatures for formation of

TABLE V Phases formed in 35.4, 56.1, 65.7, 74.9 and 83.6 at. % niobium-tin compacts at various temperatures

Annealing conditions		Composition of compact				
time	temperature	35.4 at. % Nb	56.1 at. % Nb	65.7 at. % Nb	74.9 at. % Nb	83.6 at. % Nb
1 week	925° C	Nb_3Sn Nb_6Sn_5	Nb_3Sn	Nb_3Sn	Nb_3Sn	
1 week	860° C	Nb_3Sn Nb_6Sn_5	Nb_3Sn Nb_6Sn_5	Nb_3Sn Nb_6Sn_5	Nb_3Sn Nb_6Sn_5	Nb_3Sn Nb_6Sn_5
1 week	850° C	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$?	Nb_3Sn Nb_6Sn_5 $NbSn_2$?	Nb_3Sn Nb_6Sn_5 $NbSn_2$?	Nb_3Sn Nb_6Sn_5 $NbSn_2$?
1 week	825° C	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$?	Nb_3Sn Nb_6Sn_5 $NbSn_2$?	Nb_3Sn Nb_6Sn_5 $NbSn_2$?
1 week	775° C	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$
1 week	750° C	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5? $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$?
6 weeks	650° C	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$	Nb_6Sn_5 $NbSn_2$	Nb_3Sn Nb_6Sn_5 $NbSn_2$
6 weeks	240° C	$NbSn_2$	$NbSn_2$		$NbSn_2$	$NbSn_2$

$NbSn_2$ and Nb_6Sn_5 observed in sintered compacts. The arrests were fairly reproducible in a given specimen but varied with the composition of the alloy, for example on heating the lower arrest occurred at 833 to 840° C in the 24.2, 35.4 and 45.9 at. % niobium alloys, while it occurred at 852° C in the 56.1 at. % niobium and 870° C in the 65.6 at. % niobium alloy, and the upper arrest occurred at 922° C in the 24.2, 35.4 and 45.9 at. % niobium alloys, and at 935° C in the 56.1 and 65.6 at. % niobium alloys. An impurity effect may be present here but as most of the impurities were in the niobium one might have expected the melting to have occurred at higher temperatures in the tin-rich alloys.

6. Studies of the Nb_3Sn Phase

6.1. Composition Range of Nb_3Sn in Cast Alloys

Metallographic examination of an induction-melted 74.9 at. % niobium alloy showed the microstructure consisted of Nb_3Sn with inclusions arranged in dendritic fashion inside the Nb_3Sn grains and isolated tin particles surrounded by a thin $NbSn_2$ layer on the Nb_3Sn grain-boundaries. The anodised colour of the Nb_3Sn grains varied from centre to grain-boundary. Most of the colour change occurred adjacent to the boundary in a continuous fashion indicating a concentration gradient within a single phase. Very occasionally however, especially near the specimen surface, areas were found where a sharp demarcation occurred between the centre and boundary regions of a grain suggesting that impurity segregation also existed here giving rise to the formation of another phase. The composition range of Nb_3Sn in this specimen was from 76.7 at. % niobium at grain-centres to 73.1 at. % niobium at grain-boundaries, while in another sample the grain-centres contained 80.0 at. % niobium. The composition variation from 73.1 to 80.0 at. % niobium probably reflects the composition range of Nb_3Sn at higher temperatures near the peritectic temperature.

6.2. Boundaries of the α-Niobium + Nb_3Sn Phase Field at High Temperatures

A cast 92 at. % niobium-tin alloy had a microstructure consisting of α-niobium grains with a little Nb_3Sn precipitated at the grain-boundary either as particles lying along the boundary or as squat needles nucleated at the boundary and penetrating into the α-niobium grains. The centre of three grains well away from the Nb_3Sn precipitate contained 5.6, 7.2 and 8.8 at. % tin respectively, indicating considerable solubility of tin in α-niobium at higher temperatures with the solubility limit at the peritectic temperature greater than or equal to 8.8 at. % tin. Samples of this specimen annealed for 1 day at 1495 or 1600° C showed considerable precipitation of Nb_3Sn to form a grain-boundary network and as small needles within the grains (fig. 3), the two phases occurring in about equal proportions in the 1600° C specimen. Microprobe analysis of

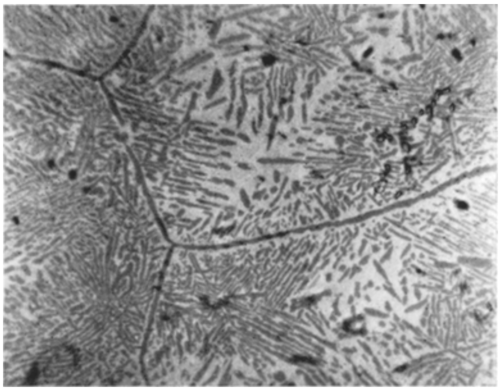

Figure 3 Nb_3Sn precipitation in a cast 92 at. % niobium-tin specimen annealed 1 day at 1495° C, anodised (× 317).

the α-niobium and Nb_3Sn showed them to contain 3.7 and 13.5 at. % tin after annealing at 1600° C and 1.1 and 16.1 at. % tin after annealing at 1495° C. These values were unreliable because of the small size of the particles and a "most likely value" based on the maximum observed value for niobium in the niobium-rich phase and for tin in the tin-rich phase (Nb_3Sn) as quoted in table IIB. This indicates that at 1600 and 1495° C the α-niobium boundary lies at 2.2 and 1.1 at. % niobium, and the Nb_3Sn boundary at 82.0 and 82.9 at. % niobium respectively.

6.3. Stability of Nb_3Sn at Low Temperatures

A sample of induction-melted 74.9 at. % niobium, the microstructure of which has been described in section 6.1 above, was sectioned and pieces annealed from 1 to 8 weeks at temperatures between 400 and 950° C. Annealing caused no significant change in the Nb_3Sn which remained segregated. Tin was still present in specimens annealed at 850° C or above, but it was not observed on annealing for 33 days at 825 or 800° C, 8 weeks at 775° C or 4 weeks at 600° C. Some tin was found after 1 week at 400 or 500° C, but the amount was considerably reduced after 1 month at 400° C, suggesting that the annealing times were too short at these temperatures to react all the tin. Nb_6Sn_5 was observed in all specimens annealed at 750 to 925° C, generally as a layer between $NbSn_2$ and the boundaries of Nb_3Sn grains. $NbSn_2$ was present in specimens annealed up to 850° C but above this temperature it was either absent or its position in the microstructure suggested it had precipitated on cooling.

These observations indicate that, although there is a slow reaction of Nb_3Sn with $NbSn_2$ or tin at lower temperatures to form Nb_6Sn_5 or $NbSn_2$, there is no evidence of any decomposition in the centre of Nb_3Sn grains and Nb_3Sn is probably stable in the absence of tin or tin-rich phases.

7. Studies of the Nb_6Sn_5 Phase

7.1. Structure of Nb_6Sn_5

A compact sintered at 850° C, showing mainly Nb_6Sn_5 on metallographic examination, was crushed and reannealed at 850° C and an X-ray powder pattern obtained by the Guinier technique. The pattern, which was very complex even after due allowance had been made for the presence of other phases, could not be indexed satisfactorily by the structure proposed by Reed, Gatos, La Fleur and Roddy [16] for Nb_3Sn_2 but agreed reasonably with the Wilhelm and Ellis [17, 18] structure. However, as the peritectic temperature differed from that reported for Nb_3Sn_2 by Wilhelm and Ellis [17, 18] and since Wyman, Cuthill, Moore, Park, and Yakowitz [9] had reported five intermediate phases in the niobium-tin system, it was decided to examine the structure of Nb_6Sn_5 by single crystal techniques.

A twin free single crystal of Nb_6Sn_5, extracted from a polished microsection of a diffusion specimen annealed at 870° C, gave an identity distance from a rotation photograph of 5.66 Å. The zero layer Weissenberg photograph could be indexed on orthogonal axes as an orthorhombic crystal with $b = 9.144$ Å and $c = 16.993$ Å. Reflections occurred on this layer for $0k0$ and $00l$ with $k, l = 2n$ and for $0kl$ with $k + l = 2n$. The crystal was remounted and rotated round the b-axis ($b = 9.2056$), and from the zero layer Weissenberg photograph values of $a = 5.649$ Å and $c = 16.868$ Å were calculated. Reflections occurred for $h00$ and $00l$ with $h, l = 2n$ and for $h0l$ with $h + l = 2n$. On the second layer reflections $h20$ and $02l$ occurred with $h, l = 2n$ and $h2l$ for $h + l = 2n$. These reflections can occur for the general case of four orthorhombic classes, i.e.

$$D_2{}^8 - I222\,,\ D_2{}^9 - I2_12_12_1\,,\ C_{2v}{}^{20} - Imm2\,,\ \text{or}\ D_{2h}{}^{25} - Immm\ .$$

7.2. Superconducting Transition Temperature of Nb_6Sn_5

Nb_6Sn_5 prepared by sintering 54 at. % niobium compacts 42 and 84 days at 870° C had superconducting transition temperatures of 1.6° K

TABLE VI Annealing experiments on cast alloys to determine the decomposition temperatures of Nb_6Sn_5 and $NbSn_2$

Composition	Previous treatment	Initial microstructure	Heat-treatment	Final microstructure (phases present and approximate percentage)
35.4 at. % Nb	as-cast	Nb_3Sn ($\sim$ 33%, but varies from 10–75%) Sn ($\sim$ 66%), thin layer $NbSn_2$ around Nb_3Sn particles	3 days 810° C	$NbSn_2$ ($\gtrsim$ 50%), Nb_3Sn ($\lesssim$50%), very little tin, no Nb_6Sn_5
			3 days 815° C	$NbSn_2$ ($\gtrsim$ 50%), Nb_3Sn ($\lesssim$ 50%), very little tin, no Nb_6Sn_5
			3 days 820° C	$NbSn_2$ ($\gtrsim$ 50%), Nb_3Sn ($\lesssim$ 50%), very little tin, no Nb_6Sn_5
			3 days 830° C	$NbSn_2$ ($\gtrsim$ 50%), Nb_3Sn ($\lesssim$ 50%), very little tin, no Nb_6Sn_5
			1 day 830° C	microprobe analysis Nb_3Sn with 75.3 at. % Nb, $NbSn_2$ with 31 at. % Nb, tin containing no Nb
46.0 at. % Nb	as-cast		3 days 820° C	Nb_3Sn ($\sim$ 67%), $NbSn_2$ ($\sim$ 33%), some free tin microprobe analysis Nb_3Sn – 76.0 at. % Nb; $NbSn_2$ – 32.0 at. % Nb; tin containing 0.1 at. % Nb (probably not significant figure)
			1 week 840° C	Nb_3Sn ($\lesssim$ 50%) Nb_6Sn_5 ($\sim$ 50%), Sn ($\sim$ 5%) containing large regular $NbSn_2$ crystals
46.0 at. % Nb	1 week 800° C	Nb_3Sn ($\sim$ 67%), $NbSn_2$ ($\sim$ 33%), a little tin	1 day 815° C	similar to initial microstructure but with less tin
			3 days 820° C	Nb_3Sn ($\sim$ 50%), $NbSn_2$ ($\sim$ 50%), thin layer of Nb_6Sn_5
			3 days 830° C	similar to initial microstructure but with no tin
			1 week 835° C	Nb_3Sn ($\sim$ 50%), $NbSn_2$ ($\sim$ 50%), thin layer of Nb_6Sn_5
			1 week 840° C	Nb_3Sn ($\sim$ 50%), Nb_6Sn_5 ($\sim$ 45%), Sn ($\sim$ 5%), a few areas of $NbSn_2$
			1 week 845° C	Nb_6Sn_5 ($\sim$ 50%), Nb_3Sn ($\sim$ 25%), Sn ($\sim$ 25%)
			1 week 850° C	Nb_6Sn_5 ($\sim$ 50%), Nb_3Sn ($\sim$ 25%), Sn ($\sim$ 25%)
			1 week 855° C	Nb_6Sn_5 ($\sim$50%), Nb_3Sn ($\sim$25%), Sn ($\sim$25%)
			1 day 880° C	Nb_6Sn_5 ($\sim$ 50%), Nb_3Sn ($\sim$ 25%), Sn ($\sim$ 25%)
56.1 at. % Nb	10 days 650° C	Nb_3Sn (> 50%), $NbSn_2$ (< 50%), no Nb_6Sn_5 microprobe analysis Nb_3Sn – 75.9 at. % Nb $NbSn_2$ – 31.4 at. % Nb	14 weeks 550° C	initial microstructure unaltered
			1 week 815° C	initial microstructure unaltered except for very thin layer of Nb_6Sn_5 between Nb_3Sn and $NbSn_2$
			1 week 820° C	initial microstructure unaltered execpt for very thin layer of Nb_6Sn_5 between Nb_3Sn and $NbSn_2$
			1 week 830° C	initial microstructure unaltered except for very thin layer of Nb_6Sn_5 between Nb_3Sn and $NbSn_2$
			1 week 840° C	initial microstructure unaltered except for layer of Nb_6Sn_5 between Nb_3Sn and $NbSn_2$
			1 week 845° C	initial microstructure unaltered except for layer of Nb_6Sn_5 between Nb_3Sn and $NbSn_2$
			1 week 847° C	Nb_6Sn_5 (> 50%), Nb_3Sn ($\sim$ 25%), remainder tin containing $NbSn_2$ precipitate
			7 h 850° C	initial microstructure unaltered except for thin layer Nb_6Sn_5 between Nb_3Sn and $NbSn_2$
			1 week 850° C	Nb_6Sn_5 (> 50%), Nb_3Sn ($\sim$ 25%), remainder tin containing $NbSn_2$ precipitate
			4 h 852° C	Nb_6Sn_5 (> 50%), Nb_3Sn ($\sim$ 25%), remainder tin containing $NbSn_2$ precipitate
			3 h 855° C	Nb_6Sn_5 (> 50%), Nb_3Sn ($\sim$ 25%), remainder tin containing $NbSn_2$ precipitate
56.1 at. % Nb	2 weeks 825° C	Nb_3Sn ($\sim$ 67%), $NbSn_2$ ($\sim$ 33%), with a thin layer of Nb_6Sn_5 between the Nb_3Sn and $NbSn_2$	4 weeks 650° C	no significant change from initial microstructure
			4 weeks 770° C	no significant change from initial microstructure
			3 days 830° C	no significant change from initial microstructure; phase composition by *microprobe* determination – Nb_3Sn – 76.8 at. % Nb, $NbSn_2$ – 31.8 at. % Nb
			8 days 845° C	no significant change from initial microstructure
			1 day 880° C	Nb_3Sn ($\sim$ 75%), Sn (5–10%), remainder Nb_6Sn_5
			1 day 900° C	Nb_3Sn ($\sim$ 75%), Sn (5–10%), remainder Nb_6Sn_5
			1 day 910° C	Nb_3Sn ($\sim$ 75%), Sn (5–10%), remainder Nb_6Sn_5
			1 day 920° C	Nb_3Sn ($\sim$ 75%), Sn (5–10%), remainder Nb_6Sn_5

TABLE VI continued

Composition	Previous treatment	Initial microstructure	Heat-treatment	Final microstructure (phases present and approximate percentage)
			1 day 930° C	Nb_3Sn (~ 75%), Sn (5–10%), remainder Nb_6Sn_5
			1 week 930° C	Nb_3Sn (~ 75%), Sn (5–10%), remainder Nb_6Sn_5
			1 week 932° C	Nb_3Sn (~ 75%), Sn (5–10%), remainder Nb_6Sn_5
			1 week 935° C	Nb_3Sn and Sn with $NbSn_2$ precipitate in the tin
56.1 at. % Nb	5 weeks at 870° C	Nb_3Sn (~ 33%), Nb_6Sn_5 (~ 67%), some tin	1 week 830° C	some $NbSn_2$ present; microprobe analysis Nb_3Sn – 74.4 at. % Nb, Nb_6Sn_5 – 52.8 at. % Nb, $NbSn_2$ – 31.7 at. % Nb
			1 week 840° C	no significant change from initial microstructure
			1 week 850° C	no significant change from initial microstructure
			1 week 925° C	no significant change from initial microstructure
			1 week 927° C	Nb_3Sn and tin
56.1 at. % Nb	thermal analysis specimen	Nb_3Sn (~ 50%), $NbSn_2$ (~ 25%), Nb_6Sn_5 (~ 12%), Sn (~ 12%)	1 month 650° C	Nb_3Sn (~ 33%), $NbSn_2$ (~ 67%), with thin layer of Nb_6Sn_5 in between
			4 weeks 770° C	Nb_3Sn (~ 50%), Nb_6Sn_5 (~ 50%), with layer of Nb_6Sn_5 in between
			1 day 910° C	Nb_3Sn ($\gtrsim$ 50%), Nb_6Sn_5 ($\lesssim$ 50%), some free tin
			1 day 920° C	Nb_3Sn ($\gtrsim$ 50%), Nb_6Sn_5 ($\lesssim$ 50%), some free tin
			1 day 930° C	Nb_3Sn ($\gtrsim$ 50%), Nb_6Sn_5 ($\lesssim$ 50%), some free tin
			1 day 935° C	Nb_3Sn and tin
65.7 at. % Nb	2 weeks 825° C	Nb_3Sn (~ 67%), $NbSn_2$ (~ 33%), with a thin layer of Nb_6Sn_5 in between microprobe analysis Nb_3Sn – 76.5 at. % Nb $NbSn_2$ – 31.8 at. % Nb	4 weeks 650° C	no significant change from initial microstructure
			4 weeks 770° C	no significant change from initial microstructure
			3 days 830° C	no significant change from initial microstructure
			1 day 900° C	Nb_3Sn, Nb_6Sn_5 and tin
			1 day 930° C	Nb_3Sn, Nb_6Sn_5 and tin
			1 day 932° C	Nb_3Sn, Nb_6Sn_5 and tin
			1 day 935° C	Nb_3Sn and tin with $NbSn_2$ precipitate in tin
60 at. % Nb	5 weeks 870° C	Nb_3Sn (~ 67%), Nb_6Sn_5 (~ 33%), with a little tin	1 week 830° C	$NbSn_2$ present in specimen
			1 week 840° C	$NbSn_2$ present in specimen
			1 week 850° C	no significant change from initial microstructure
			1 week 920° C	no significant change from initial microstructure
			1 week 923° C	no significant change from initial microstructure
			1 week 925° C	Nb_3Sn and tin
			1 week 930° C	Nb_3Sn and tin

(width 1.2° K) and 1.5° K respectively, while crystals of Nb_6Sn_5 grown by diffusion for 7 days at 870° C had a superconducting transition temperature of 2.07° K (width 0.25° K). Crystals of $NbSn_2$ were also produced in this diffusion experiment and showed a sharp superconducting transition at 2.68° K. This work has been reported by Charlesworth [13].

7.3. Peritectic Temperature of Nb_6Sn_5

The metallographic observations used to determine this temperature in cast alloys of 56.1 and 65.7 at. % niobium are shown in table VI.

Initially samples which had been annealed for 5 weeks at 870° C to give a microstructure consisting of Nb_3Sn and Nb_6Sn_5 with a little free tin, were examined. There was virtually no change in the microstructure after 1 week's annealing at temperatures up to 923° C for the 65.7 at. % alloy and 925° C for the 56.1 at. % alloy, but all the Nb_6Sn_5 had disappeared leaving Nb_3Sn and tin after 1 week's annealing at 925 and 927° C respectively. A higher value of the peritectic temperature was found for samples which had been treated for 2 weeks at 825° C. The structure consisted initially of Nb_3Sn and $NbSn_2$ with Nb_6Sn_5 present only as a thin layer between the other two phases. More Nb_6Sn_5 as well as some tin was produced on annealing at higher temperatures, and this was present in both alloys after 1 week at 932° C but it had disappeared after 1 week at 935° C. Similarly in a sample of the 56.1 at. % niobium alloy which had been used for thermal analysis experiments where an arrest at ~ 935° C had been found on the heating curves, Nb_6Sn_5 was present in the microstructure after 1 day at 930° C but was absent after 1 day at 935° C.

The scatter in these results is larger than one would anticipate from temperature fluctuations in the annealing furnaces, or from gradients across the tube diameter, and no clear correlation with purity difference in the starting material emerged.

8. Studies of the $NbSn_2$ Phase

8.1. Structure of $NbSn_2$

The diffraction pattern taken on a Guinier camera from powder obtained by sintering at 500° C, crushing and reannealing at 500° C was complex and could not adequately be explained by the Nb_2Sn_3 structure proposed by Reed, Gatos, La Fleur and Roddy [16], although the compact had been predominantly $NbSn_2$. A single crystal of $NbSn_2$ extracted from the tin of a diffusion sample annealed 5 weeks at 770° C was consequently examined. The identity distance for the *b*-axis determined from rotation photography was 5.64 Å and the zero layer Weissenberg photograph could be indexed on orthogonal axes with $a = 9.838$ Å and $c = 19.163$ Å. No accurate lattice parameter determination was attempted. Reflections of the type *h*00 and 00*l* occurred for *h* or *l* equal to 4*n* suggesting the structure must belong to one of the orthorhombic space groups C_{2v}^{19} – *Fdd*2 or D_{2h}^{24} – *Fddd*. Wilhelm and Ellis [17, 18] determined the space group to be D_{2h}^{24} – *Fddd*. Reflections *h*0*l* were found for $h, l = 4n$ or for $h = 4n + 2, l = 2n + 1$. The latter are forbidden reflections for the space group D_{2h}^{24} – *Fddd* with atoms in the general positions, or equally in the special positions determined by Gomes de Mesquita, Langereis, and Leenhouts [19]. The pattern of reciprocal lattice spots deduced from the zero layer Weissenberg photograph was the same as that for a crystal with space group D_{2h}^{24} – *Fddd* rotated around $[\bar{1}10]$. A twin of a crystal rotated around [010] could have this axis parallel to the rotation axis if the following relations held $[001]_M//[001]_T$, $[010]_M//[110]_T$ and $[100]_M//$ to the normal to $[110]_T$. The [130] direction lies 22 min from the normal to the (110) plane and the twin plane would be only 5½ min from $(3\bar{1}0)$ if the lattice parameters derived by Van Vucht, Van Ooijen, and Bruning [20] are used to calculate these angles. The explanation is not completely satisfactory since the reciprocal spacings of 400 and 220 differ by about half a percent so if the matrix and twin reciprocal lattices were superimposed as suggested, these spots should be separated by more than twice the $\alpha_2 - \alpha_1$ doublet separation which alone is evident on the photograph. Also no twin layer lines were found on the rotation photograph, and the absence of the permitted *h*0*l* reflections with $h, l = 4n + 2$ is puzzling.

The crystal was unfortunately lost while being remounted for rotation around a different axis so another crystal produced in a diffusion specimen annealed at 870° C was examined. The *a*-axis spacing determined from a rotation photograph was 9.845 Å and a zero layer Weissenberg was indexed with parameters $b = 5.644$ Å and $c = 19.215$ Å. Reflections on this layer occurred for 0*k*0 and 00*l* with $k, l = 4n$ and for 0*kl* for $k, l = 2n$. On the first and third layers reflections of the type *hkl* were found for $k, l = 2n + 1$.

These reflections are all consistent with a space group D_{2h}^{24} – *Fddd.*

8.2. Superconducting Transition Temperatures of $NbSn_2$

This has been reported by Charlesworth [13]. A sample of $NbSn_2$ prepared by sintering a 33 at. % niobium compact for 84 days at 627° C had a superconducting transition temperature of 1.89° K (width 0.2° K) measured by an inductive method. A sharper transition (width 0.05° K) at a higher temperature of 2.65° K was measured for $NbSn_2$ crystals grown in tin in a diffusion sample annealed 10 days at 600° C. In a sample prepared from a diffusion experiment after 7 days at 870° C where Nb_6Sn_5 crystals were also present a transition temperature of 2.68° K was measured.

8.3. Peritectic Temperature of $NbSn_2$

The peritectic temperature of $NbSn_2$ was determined from metallographic observations on cast alloys containing 35.4, 46.0, 56.1 and 65.7 at. % niobium. The phases were identified from the anodised colours, and in a few cases the compositions of the phases were determined by electron microprobe methods. These metallographic observations are summarised in table VI. $NbSn_2$ is definitely formed at 840° C and appears unstable above 845° C except in one specimen annealed at 850° C where it was still present after 7 h. The peritectic temperature of $NbSn_2$ was taken to be 845 ± 7° C from these results.

9. Discussion

No significant quantity of niobium was found dissolved in tin even in specimens annealed at 1400° C but since $NbSn_2$ formed so rapidly on cooling and was found in the tin in samples annealed above about 850° C some small solubility of niobium in liquid tin obviously occurred. This would be consistent with the low solubility of niobium in tin at low temperatures shown by the liquidus curves of Ellis [18] and Vieland [21] and the fewer experimental points obtained by Van Vucht, Van Ooijen, and Bruning [20] and Kogan, Krivko, Lazarev, Lazareva, Matsakova, and Ovcharenko [22].

Apart from the three phases Nb_3Sn, Nb_6Sn_5 and $NbSn_2$ there was evidence of a fawn-coloured phase precipitating at low temperature which seemed to be marginally richer in tin than $NbSn_2$ but this is doubtful because of the small size of the particles. Possibly a niobium-tin phase containing impurity atoms has precipitated in these cases. However, Enstrom, Courtney, Pearsall, and Wulff [23] found $NbSn_2$ by X-ray and metallographic methods in samples annealed at 250° C so the formation of $NbSn_2$ at the slightly lower temperature of 240° C would not be remarkable.

The $NbSn_2$ phase showed compositions between 31.0 and 34.0 at. % niobium with an average composition of 32.1 at. % niobium, slightly richer in tin than the stoichiometric composition. As the accuracy of composition determination was of the order ± 1 at. % niobium, the phase may be regarded as stoichiometric with no great composition range. Levinstein and Buehler [24] report that $NbSn_2$ is stoichiometric, Van Vucht, Van Ooijen, and Bruning [20] found the composition to be 33.0 ± 0.5 at. % niobium by chemical analysis, Barber and Giles [25] found by microprobe analysis that it had a composition range 32.3 to 34.5 at. % niobium, and Kuznetsova, Kovaleva, and Beznosikova [26] report that it contains about 33.5 at. % niobium. Most other investigators find the phase to contain more niobium than the stoichiometric composition – Enstrom, Pearsall, and Wulff [27] find 35 to 40 at. % niobium, Wyman, Cuthill, Moore, Park and Yakowitz [9] 39 to 41.3 at. % niobium, Rinderer, Wurm, Züllig, and de Beer [28] 39.5 to 40.2 at. % niobium, Tachikawa and Fukuda [29] 38.4 to 42.3 at. % niobium, Ellis [18] 43.7 at. % niobium, and Kogan, Krivko, Lazarev, Lazareva, Matsakova, and Ovcharenko [30] 50 at. % niobium. Some of this variation is clearly due to systematic errors in the analysis, but a genuine composition range possibly occurs since, for example, Rosenbaum and Schadler [31] reported the composition of a single crystal to be 33.8 ± 1 at. % niobium but the phase in a polyphase sample contained 38.4 to 37.3 at. % niobium.

$NbSn_2$ was found to be orthorhombic, the average parameters of two crystals being 9.84, 5.64 and 19.19 Å. No refinement of parameters was attempted but these values are quite close to those determined by Ellis and Wilhelm [32] 9.860, 5.655, and 19.152 Å, by Gomes de Mesquita, Langeris and Leenhouts [19] 9.860, 5.6477, and 19.127 Å, by Enstrom, Pearsall, and Wulff [27] 9.86, 5.64, and 19.13 Å, by Levinstein and Buehler [24] 9.85, 5.63, and 18.96 Å, and by Kuznetsova, Kovaleva, and Beznosikova [26] 9.85, 5.65, and 19.2 Å. The reflections from the crystal grown at 870° C are consistent with those from the space group D_{2h}^{24} – *Fddd* determined by Wilhelm and Ellis [17, 18] and Gomes de Mesquita, Langereis, and Leenhouts [19]. With the crystal grown at 770° C additional reflections of type $h0l$ with $h = 4n + 2$, $l = 2n + 1$ were present but those with $h, l = 4n + 2$ were absent. The additional spots might be explained by twinning on {130}. It is interesting that Enstrom, Pearsall, and Wulff [33] reported that although the same lines and lattice spacings were observed from crystals grown at 750 and 550° C the intensities were different. They attributed this to the different compositions of the specimens formed at 550 and 750° C (40 at. % niobium and 35 at. % niobium respectively) with atoms occupying different positions. As the crystals used in the present work were not analysed it is possible they contained different amounts of impurities, e.g. oxygen or hydrogen. However, the superconducting transition temperature of $NbSn_2$ crystals appeared to be fairly constant. Those extracted from a diffusion run of 10 days at 600° C had $T_c = 2.65°$ K and width 0.05° K, while those from a specimen annealed 7 days at 870° C had $T_c = 2.68°$ K with width 0.03° K. These values lie between values of 2.60° K reported by Van Ooijen, Van Vucht, and Druyvesteyn [34] and 2.70° K reported by Kogan, Krivko, Lazarev, Lazareva, Matsokova, and Ovcharenko [30]. In a sintered sample a broader transition at a lower temperature was found – $T_c = 1.89°$ K, width 0.2° K – and this lowering may be due to the greater impurity content (mainly oxygen) of the starting material. Enstrom, Pearsall, and Wulff [33] found a range of superconducting transition temperatures in sintered samples but at slightly higher temperatures – 2.4 to 3.4° K.

The peritectic temperature of $NbSn_2$ was determined as 845 ± 7° C by metallographic observation. Values reported in the literature range from 820 ± 3° C by Ellis [18] to 950 ± 10° C by Levinstein and Buehler [24], though this higher value may be due to $NbSn_2$ precipitated on cooling being mistaken for $NbSn_2$ formed at temperature. Temperatures closer to our value were found by Rosenbaum and Schadler [31] at 840 ± 12° C, by Van Vucht, Van Ooijen, and Bruning [20] at 840 ± 10° C, by Kuznetsova, Kovaleva, and Beznosikova [26] at 840 ± 10° C and by Enstrom, Pearsall, and Wulff [27] at 850° C. Kogan, Krivko, Lazarev, Lazareva, Matsakova, and Ovcharenko [30] also regard this phase (NbSn) as unstable above 850° C. Slightly higher peritectic temperatures have been reported by Svechnikov, Pan, and Beletskii [35] at 860 ± 10° C, by Wyman Cuthill, Moore, Park, and Yakowitz [9] at 863 ± 5° C, and by Barber and Giles [25] at 880 ± 15° C.

As $NbSn_2$ was found to form at 400° C and probably also at 240° C it appears to be stable to low temperatures. This view is generally held and is supported by published evidence; e.g. Barber and Giles [25] found $NbSn_2$ in diffusion specimens annealed 300 h at 450° C, and in powder compacts it has been observed after 3 days annealing at 440° C by Reed, Gatos, La Fleur and Roddy [16], after 1½ h at 400° C by Coles, Corsan, Buxton, and Lewis [36], and after annealing at 250° C by Enstrom, Courtney, Pearsall, and Wulff [23].

The mean niobium content of Nb_6Sn_5 determined in these experiments was 53.7 at. % which is slightly richer in tin than the stoichiometric composition but probably not significantly so. The composition ranged from 52.8 to 54.1 at. % niobium indicating a narrow phase field. Barber and Giles [25] report Nb_6Sn_5 to be stoichiometric, Van Vucht, Bruning, and Donkersloot [37] report it to contain 54 ± 2 at. % niobium, and Enstrom, Pearsall, and Wulff [27] found it contained 54.5 at. % niobium by chemical and 56.1 at. % niobium by microprobe analysis. Other determinations have found Nb_6Sn_5 to be richer in niobium than the stoichiometric composition – Enstrom, Courtney, Pearsall, and Wulff [23] report 56.1 at. % to 58 at. % niobium, Kuznetsova, Kovaleva, and Beznosikova [26] about 58 at. % niobium, Rinderer, Wurm, Züllig, and de Beer [28] 58.5 ± 1.5 at. % niobium, Tachikawa and Fukuda [29] 58.5 to 61.0 at. % niobium, Rosenbaum and Schadler [31] 59.3 ± 1.0 at. % niobium. None of these determinations suggest any extensive composition range for the phase though the individual values span the composition range 54.5 to 61.0 at. % niobium. The differences probably reflect systematic errors in chemical and microprobe analysis.

The structure of Nb_6Sn_5 was orthorhombic with average parameters of 5.65, 9.17, and 16.93 Å. No parameter refinement was attempted but the values are similar to those found by Ellis and Wilhelm [32] (5.656, 9.199, and 16.843 Å), by Van Vucht, Bruning, and Donkersloot [37] (5.6549, 9.2057, and 16.814 Å) and Enstrom [38] (5.656, 9.212, and 16.80 Å). The superconducting transition temperature of crystals grown at

870° C was 2.07° K (width 0.25° K) and in samples sintered at 870° C for 42 and 84 days was 1.6° K (width 1.2° K) and 1.5° K respectively. The difference between the crystals and the sintered specimens was attributed to the greater impurity content of the compacts. Neglecting the earlier determinations which reported that Nb_6Sn_5 had a superconducting transition temperature above 16° K, three determinations give quite different results: Enstrom [38] found $T_c = 2.8°$ K (width about 0.4° K), Schadler and Rosenbaum [39] $T_c = 2.37°$ K, and Van Vucht, Van Ooijen, and Bruning [20] $T_c < 0.3°$ K. Enstrom [38] was uncertain whether a layer of $NbSn_2$ covering some of the crystals affected his determination. In the present work $NbSn_2$ crystals were present with the Nb_6Sn_5 but they gave a sharp transition temperature of 2.68° K.

The peritectic temperature of Nb_6Sn_5 was found to be 930 ± 8° C. Values reported in the literature range from 910 ± 10° C by Kuznetsova, Kovaleva, and Beznosikova [26] to 950 ± 15° C by Barber and Giles [25]. Temperatures closer to our value are 915 ± 5° C found by Ellis [18], 912 ± 12° C by Rosenbaum and Schadler [31], 920 ± 10° C by Svechnikov, Pan, and Beletskii [35], 925° C by Enstrom, Pearsall, and Wulff [27] and 930 ± 15° C by Van Vucht, Van Ooijen, and Bruning [20]. Wyman, Cuthill, Moore, Park, and Yakowitz [9] also report a thermal arrest at 922 ± 5° C.

Nb_6Sn_5 has been observed to form in a compact annealed at 500° C, and is probably stable at low temperatures although very slow to form. Enstrom, Courtney, Pearsall, and Wulff [23] have found Nb_6Sn_5 in compacts annealed 16 h at 700° C, and Ellis and Wilhelm [32] and Van Vucht, Van Ooijen, and Bruning [20] showed that X-ray patterns from Nb_6Sn_5 were unchanged after annealing 3 days at 550° C and 4 h at 400° C respectively.

The tin-rich composition for Nb_3Sn produced in compacts and diffusion experiments below 1400° C was 72.6 to 73.3 at. % niobium, and the boundary region of Nb_3Sn grains in cast specimens has a composition in this range, Hanak, Cody, Aron and Hitchcock [40] reported vapour-deposited Nb_3Sn containing 73.3 at. % niobium and diffusion layers or crystals grown in tin can be richer in tin than the stoichiometric composition; e.g. Maier and Wilhelm [41] report a crystal containing 72.8 at. % niobium, and Barber and Giles [25] report a diffusion zone containing 73.7 at. % niobium. Vieland [21] shows compositions of about 74.4 and 73.7 at. % niobium on his equilibrium diagram but he thought the results were spurious as tin-rich phases may have been included with the crystals analysed.

The niobium-rich boundary of Nb_3Sn was not attained in compacts or diffusion specimens annealed below 1400° C. In cast alloys some grain-centres contain 80 at. % niobium, and the composition of the Nb_3Sn precipitated on annealing α-niobium at 1495 or 1600° C lay between 82 and 83 at. % niobium. Courtney, Pearsall, and Wulff [42] note the appearance of an α-niobium precipitate in samples containing more than 82.5 at. % niobium and Vieland [21] sets his niobium-rich boundary at about 82 at. % niobium. Courtney, Pearsall, and Wulff [42] suggest that a defect structure based on Nb_3Sn may extend to niobium compositions greater than 92 at. % niobium, and Svechnikov, Pan and Beletskii [43] show a much wider homogeneity range for Nb_3Sn than Vieland [21]. However, the lattice parameters encountered in these investigations are similar and it is shown in reference [2] that, if the same lattice parameter composition relation is used to determine the phase compositions, the results of these investigations lie in a phase field similar to that determined by Vieland [21].

Since Nb_3Sn has been found in a compact annealed 3 months at 627° C and a cast 74.9 at. % niobium alloy has shown little metallographic change on annealing for one month at 400° C, it is thought that the phase is stable to low temperatures. Ellis [18] and Enstrom [38] showed that Nb_3Sn could form in diffusion samples annealed 162 h at 640 and 120 h at 600° C respectively, and it has been produced on a substrate at 280° C by simultaneous evaporations of niobium and tin by Fowler [44].

The solubility of tin in niobium was found to diminish from about 8.8 at. % niobium at the Nb_3Sn peritectic temperature to about 2.2 at. % niobium at 1600° C and 1.1 at. % niobium at 1495° C. No tin pick-up in the niobium particles in compacts sintered below 950° C was observed. This apparent lack of solubility of tin in niobium in diffusion experiments has also been reported by Coles, Corsan, Buxton, and Lewis [36], and by Bode and Uzel [45] and by Maier [46]. The latter authors [45, 46] think that these results follow from the kinetics of the reaction and do not indicate the true solubility of tin in solid niobium. If this is the case the solubility of tin in niobium will have been underestimated in preparing the present equilibrium diagram. However, the observation by Coles, Corsan, Buxton, and Lewis [36] that oxygen solution could cause the lattice parameter and hardness changes which have been attributed to tin in solid solution is important and solubility determinations relying on either of these measurements may be suspect.

10. Niobium-Tin Equilibrium Diagram

Fig. 4 is the equilibrium diagram constructed from our evidence for the composition and stability of the various phases investigated. This is in general agreement with the diagrams produced by Ellis [18], Van Vucht, Van Ooijen, and Bruning [20] and Rosenbaum and Schadler [31]. It differs from the diagrams of Reed, Gatos, La Fleur and Roddy [16], Enstrom, Courtney, Pearsall, and Wulff [23] (modified with the peritectic temperatures later reported by Enstrom, Pearsall, and Wulff [27]), Barber and Giles [25], and Kuznetsova, Kovaleva, and Beznosikova [26] chiefly in showing the phases Nb_3Sn and/or Nb_6Sn_5 to be stable to low temperatures. Levinstein and Bühler's diagram [24] would agree if similarly modified and if the peritectic temperature of $NbSn_2$ were lowered by 100° C. Agreement with the diagrams of Agafonova, Baron, and Savitskii [3], Wyman, Cuthill, Moore, Park, and Yakowitz [9], Kogan, Krivko, Lazarev, Lazareva, Matsakova, and Ovcharenko [30], and Svechnikov, Pan, and Beletskii [35] is less good, though there is much experimental work in these papers which agrees with our findings. Little work has been done in the higher temperature range studied by Vieland [21] but his conclusions about the shape of the Nb_3Sn phase field appear correct.

It is perhaps surprising that there is so much agreement between these workers since the purities of the starting materials varied greatly and since many of the annealing times used were obviously too short to achieve equilibrium at low temperatures. Probably even when fairly pure starting materials were employed contamination during sample preparation and annealing occurred and all the diagrams refer to niobium-tin

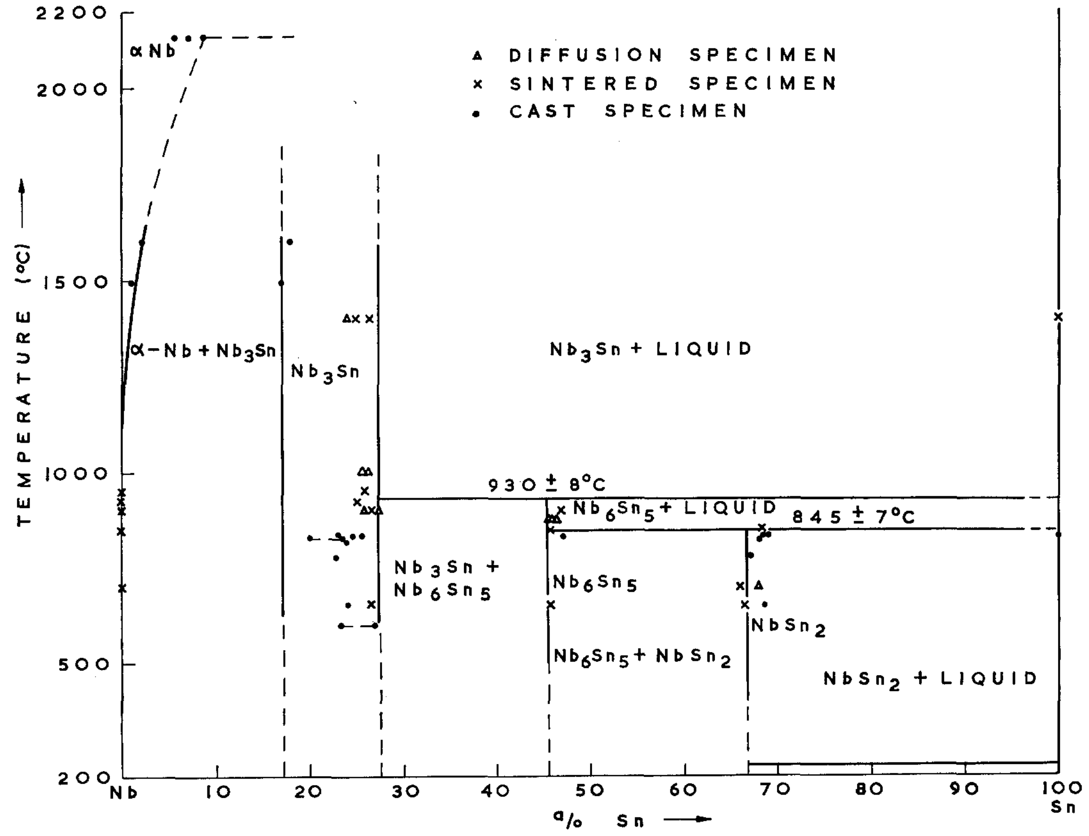

Figure 4 Composition and temperature ranges of phases found in the niobium-tin system.

alloys with a fairly high oxygen content. The existing diagrams are probably quite adequate for interpretation of (say) the microstructure of sintered samples, but should very pure starting materials and very clean heat-treatment conditions become common in the future, further redeterminations of the diagram may become necessary.

In fig. 5 the data from the present work has been combined with information from other sources. As with other attempts of this kind [20, 47] it relies very largely on Vieland [21] for the high-temperature portion of the diagram.

The α-niobium solidus is based on Agafonova, Baron, and Savitskii's [3] determination although the melting point of niobium has been taken at a higher value 2468° C from Schofield's work [48]. The peritectic temperature of 2130° C comes from determinations by Ellis [18] and Vieland [21]. The solubility of tin in niobium at this temperature is taken at 9 at. % tin from the present work; this value also lies between values of 8 at. % tin reported by Van Vucht, Van Ooijen, and Bruning [20] and 10 at. % tin reported by Bachner, Gatos, and Banus [49]. The α-niobium boundary at lower temperatures is derived from the present work and the observation by Coles, Corsan, Buxton, and Lewis [36] of negligible tin solubility at 1125° C.

The Nb_3Sn phase field is based on Vieland's determination [21] except for the extension of the niobium-rich boundary to 82.5 at. % niobium at 1500° C, and of the tin-rich boundary to 74 at. % niobium. The latter may be in error by ± 1 at. % niobium as some composition determinations in the present and other work show Nb_3Sn containing ~ 73 at. % niobium, while several published graphs of property

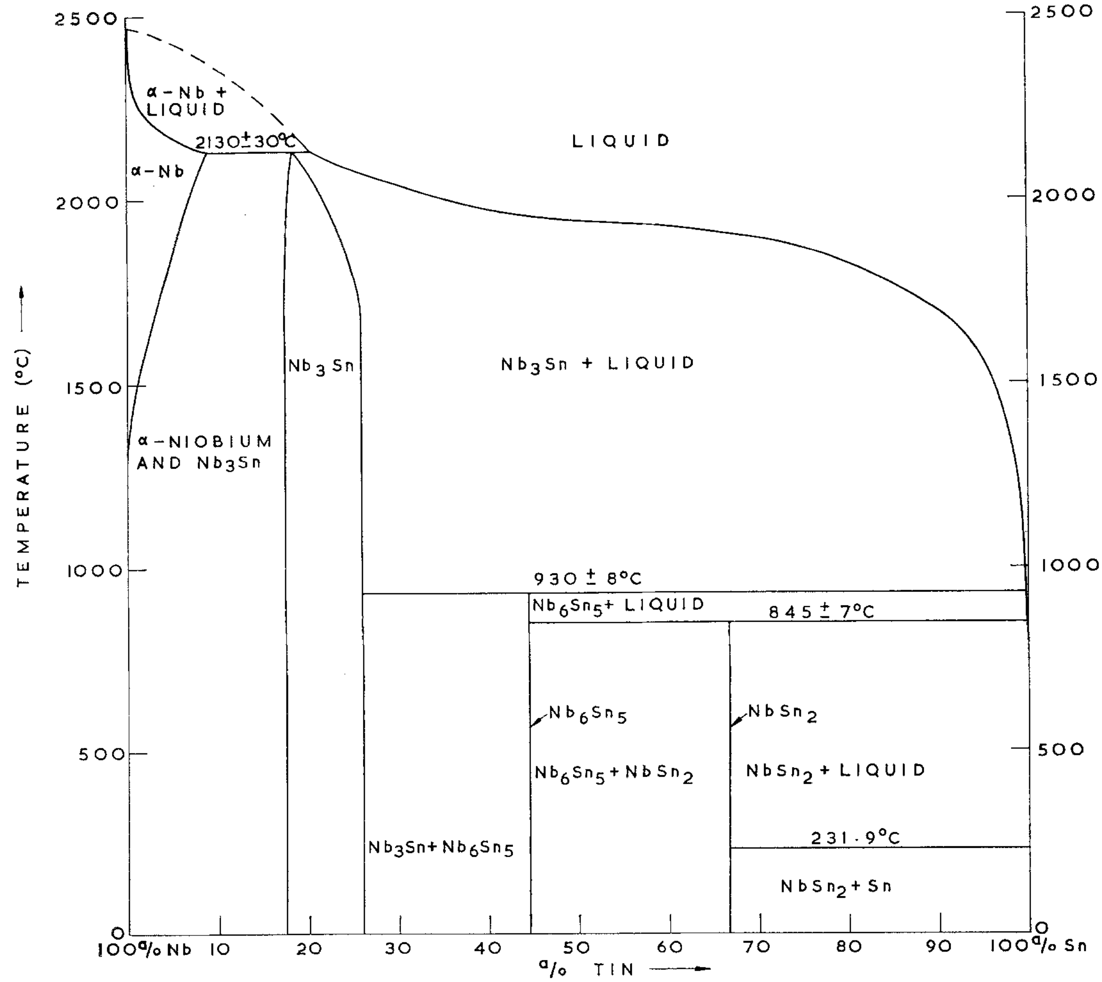

Figure 5 Niobium-tin equilibrium diagram.

versus composition show the composition range of the phase extending only on the niobium-rich side of the stoichiometric composition.

Nb_6Sn_5 and $NbSn_2$ are shown as stoichiometric with no composition range, and the peritectic temperatures are taken from the present work. The solubility of niobium in solid tin is taken as nil and the $NbSn_2$-tin eutectic is drawn at the melting point of tin. There is no experimental work on the liquidus above the Nb_3Sn peritectic. Below the Nb_3Sn peritectic the liquidus follows Vieland [21] up to 87 at. % tin with the tin-rich portion obtained by combining Vieland's [21] and Ellis' [18] results which show a linear dependence of liquidus temperature on the logarithm of niobium concentration [2].

Acknowledgement

The authors would like to thank Mr C. H. Thomas and Mr D. Armstrong for specimen preparation and heat-treatment, Mr R. M. Crispin for assistance in some diffusion experiments and Mr F. Haines for metallographic preparation. They are grateful to Mr E. Jackson for single crystal photographs of one specimen, to Mr M. S. W. Webb for analyses, and to Dr D. M. Poole, Mrs P. M. Martin and Mr J. L. Shaw for microprobe analyses. They would like to thank Mr A. C. Barber and Mr R. D. Giles of Imperial Metal Industries Ltd, Birmingham, for permission to quote from their unpublished research. They would also like to thank Professor M. B. Waldron, Dr D. M. Poole and Dr B. W. Howlett for encouragement and advice.

References

1. J. E. KUNZLER, E. BUEHLER, F. S. L. HSU, and J. H. WERNICK, *Phys. Rev. Lett.* **6** (1961) 89.
2. P. E. MADSEN, to be published.
3. M. I. AGAFONOVA, V. V. BARON, and E. M. SAVITSKII, *Izv. Akad. Nauk SSSR Otdel tekh Nauk Metall Toplevo* **5** (1959) 138.
4. P. E. MADSEN, J. P. CHARLESWORTH, I. MACPHAIL, and M. B. WALDRON, unpublished work.
5. I. MACPHAIL, AERE R6006 (1969).
6. D. ARMSTRONG, P. E. MADSEN, and E. C. SYKES, *J. Nucl. Matls.* **2** (1959) 127.
7. M. L. PICKLESIMER, ORNL-2296 (1957).
8. *Idem, Appl. Phys. Lett.* **1** (1962) 64.
9. L. L. WYMAN, J. R. CUTHILL, G. A. MOORE, J. J. PARK, and H. YAKOWITZ, *J. Res. NBS* **66A** (1962) 351.
10. I. MACPHAIL, AERE R5421 (1967).
11. P. M. THOMAS, AERE R4593 (1964).
12. J. L. SHAW, AERE R6071 (1969).
13. J. P. CHARLESWORTH, AERE R5198 (1966); *Phys. Lett.* **21** (1966) 501.
14. S. J. LLOYD and J. R. MURRAY, *J. Sci. Inst.* **35** (1958) 252.
15. C. F. OLD and I. MACPHAIL, AERE R5513 (1967); *J. Mater. Sci.* **4** (1969) 202.
16. T. B. REED, H. C. GATOS, W. J. LA FLEUR, and J. T. RODDY, "Superconductors", edited by M. Tannenbaum and M. V. Wright. Proceedings of AIME conference held at New York, 18 February 1962 (Interscience, New York, 1962) p. 143.
17. H. WILHELM and T. G. ELLIS, Ames Rep. IS-500 (1962).
18. T. G. ELLIS, "Niobium-tin-aluminium Alloy Studies", thesis, Iowa State University of Science and Technology, Ames, Iowa (1962).
19. H. H. GOMES DE MESQUITA, C. LANGEREIS, and J. I. LEENHOUTS, *Philips Res. Reports* **18** (1963) 377.
20. J. N. H. VAN VUCHT, D. J. VAN OOIJEN, and H. A. C. M. BRUNING, *ibid* **20** (1965) 136.
21. L. J. VIELAND, *RCA Review* **25** (1964) 366.
22. V. S. KOGAN, A. I. KRIVKO, B. G. LAZAREV, L. C. LAVAREVA, A. A. MATSAKOVA, and O. N. OVCHARENKO, *Fiz. Metal. i Metalloved.* **15** (1963) 143.
23. R. E. ENSTROM, T. COURTNEY, G. PEARSALL, and J. WULFF, "Metallurgy of Advanced Electronic Materials", edited by G. E. Brock. Proceedings of AIME conference held at Philadelphia, 27-29 August 1962 (Interscience, New York, 1963) p. 121.
24. H. J. LEVINSTEIN and E. BUEHLER, *Trans. AIME* **230** (1964) 1314.
25. A. C. BARBER and R. D. GILES, (Imperial Metal Industries) private communication (1965).
26. V. G. KUZNETSOVA, V. A. KOVALEVA, and A. V. BEZNOSIKOVA, *Metalloved Fiz-Khim Metalfiz Sverkhprovodnikov* (1967) 146.
27. R. E. ENSTROM, G. W. PEARSALL, and J. WULFF, *J. Metals* **16** (1964) 97.
28. L. RINDERER, J. WURM, W. ZÜLLIG, and Z. DE BEER, *Z. Phys.* **179** (1964) 407.
29. K. TACHIKAWA and S. FUKUDA, *J. Jap. Inst. Metals* **29** (1965) 1125.
30. V. S. KOGAN, A. I. KRIVKO, B. G. LAZAREV, L. C. LAZAREVA, A. A. MATSAKOVA, and O. N. OVCHARENKO, *Tr. Soveschch. po. Metalloved. i. Metallafiz Sverkhprovodnikov* 1st, Moscow 1964 (pub. 1965) p. 76.
31. H. S. ROSENBAUM and H. W. SCHADLER, "The Electron Microprobe", edited by T. D. McKinley, K. J. F. Heinrich, and D. B. Wittry. Proceedings of Electrochem. Soc. Meeting, Washington, DC, October 1964 (Wiley & Sons, New York, 1966) p. 512.
32. T. G. ELLIS and H. WILHELM, *J. Less-Comm. Met*, **7** (1964) 67.
33. R. E. ENSTROM, G. W. PEARSALL, and J. WULFF, *Appl. Phys. Lett.* **3** (1963) 81.
34. D. J. VAN OOIJEN, J. H. N. VAN VUCHT, and W. F. DRUYVESTEYN, *Phys. Lett.* **3** (1962) 128.

35. V. N. SVECHNIKOV, V. M. PAN, and Y. P BELETSKII. *Doklady Akademmi Nauk SSSR* **173** (1967) 110.
36. G. W. COLES, J. M. CORSAN, A. BUXTON, and B. LEWIS, *J. Less-Comm. Met.* **8** (1965) 402.
37. J. H. N. VAN VUCHT, H. A. C. M. BRUNING, and A. C. DONKERSLOOT, *Phys. Lett.* 7 (1963) 297.
38. R. E. ENSTROM, *J. Appl. Phys.* **37** (1966) 4880.
39. H. W. SCHADLER and H. S. ROSENBAUM, Annual meeting of Amer. Inst. of Met. Engineers (Feb. 1964) mentioned in [38].
40. J. J. HANAK, G. D. CODY, P. R. ARON, and H. C. HITCHCOCK, "High Magnetic Fields". Proceedings of int. conf. held at MIT, Cambridge, Mass, 1-4 November 1961 (MIT Press/John Wiley, 1962) p. 592.
41. R. G. MAIER and G. WILHELM, *Z. Naturforsch.* **19a** (1964) 399.
42. T. H. COURTNEY, G. V. PEARSALL, and J. WULFF, *Trans. AIME* **233** (1965) 212.
43. V. N. SVECHNIKOV, V. M. PAN, and Y. P. BELETSKII, *Doklady Akademii Nauk SSSR* **166** (1966) 1388.
44. P. FOWLER, NASA report N65 17508 (1963).
45. H. J. BODE and Y. UZEL, *Phys. Lett.* **24A** (1967) 141.
46. R. G. MAIER, *Z. Metallk.* **57** (1966) 874.
47. F. A. SHUNK, "Constitution of Binary Alloys", second supplement (McGraw-Hill, New York, 1969) p. 203.
48. T. H. SCHOFIELD, *J. Inst. Met.* **85** (1957) 372.
49. F. J. BACHNER, H. C. GATOS, and M. B. BANUS, *Trans. AIME* **233** (1965) 277.

Received 23 March and accepted 20 April 1970.