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THE THERMAL CYCLING OF Nb–NbSn$_2$ AND Nb–Sn POWDER COMPACTS

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ABSTRACT

Various Nb–Sn and Nb–NbSn$_2$ powder mixtures have been thermally cycled over the temperature range 650–1000°C in a differential thermal analysis unit to determine the alloying behaviour of the powders and to determine data that might be of use in the assessment of the various versions of the Nb–Sn phase diagram. Only the low % Sn mixtures were found to approach their equilibrium states during the cycling. Mixtures high in Sn segregated into separate tin-rich and niobium-rich layers. NbSn$_2$ was found to decompose during cycling to yield Nb$_3$Sn and Sn because of the very slow kinetics of the peritectic reactions by which Nb$_6$Sn$_5$ and NbSn$_2$ are formed during the cooling part of the thermal cycle.

INTRODUCTION

Amongst the A15 structure superconducting compounds Nb$_3$Sn still maintains its position as the most widely used commercial material. Because of its brittle nature Nb$_3$Sn cannot be mechanically worked to produce a finished superconducting component, instead the component is produced from a suitable niobium and tin-containing composite by a diffusion–annealing heat treatment after the component has been manufactured. Although the early "Kunzler wire" relied upon the diffusion annealing of a mixture of elemental niobium and tin powders contained in a drawn niobium tube [1], tin in its elemental form is not the most suitable tin source because of its low melting point. A solid-state diffusion process is preferred for the formation of Nb$_3$Sn because of the industrial production difficulties associated with the presence of a liquid phase within a heavily-worked composite material during the necessary diffusion–annealing heat treatment. Current processes rely upon the use of tin sources of higher melting point; α-bronze in the "bronze route" [2] and NbSn$_2$ in the "ECN-route" [3]. Optimization of these processes depends upon the understanding of the relevant part of the Nb–Sn–Cu ternary system and of the mechanism of diffusion–annealing of bronze–Nb or Nb–NbSn$_2$ (plus Cu) powder composites.

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Despite the numerous papers concerning Nb_3Sn that have been published over recent years and have been subjected to a number of reviews [4,5] there is surprisingly little information available on the ternary system, although work by Hopkins et al. (6), Zwicker and Rinderer [7] and Zwicker et al. [8] has attempted to alleviate this situation. In addition, although the binary Nb–Sn system has been the subject of many studies [9–13] there still remain a number of important discrepancies that are worthy of consideration.

The present study using differential thermal analysis (DTA) and X-ray diffraction analysis was undertaken to gain an understanding of phase formation and phase stability during the heating and cooling of niobium–tin and niobium–$NbSn_2$ powder mixtures in order to explain observations made during the diffusion–annealing of powder compacts. It was further anticipated that once the powder reactions in the binary system had been characterised the study could be extended to the ternary system containing copper and so provide constitutional data of use in the commercial production processes. In addition to these aims of the present study it was also anticipated that the DTA study might provide evidence for the causes of the disagreement in the literature concerning the binary Nb–Sn phase diagram because a number of the earlier workers had attempted to use DTA, in conjunction with other techniques, for their studies of this system.

EXPERIMENTAL PROCEDURE

Materials

The niobium and $NbSn_2$ powders, having particle sizes of approximately 2 μm and 1 μm, respectively, were obtained from Cerac Pure Inc. and the tin powder, of 99.98% purity, was supplied by BDH Chemicals Ltd. The analyses of the Nb and $NbSn_2$ powders are given in Table 1. Although the $NbSn_2$ powder was stated to be pure, differential scanning calorimetry of the sample showed a significant fusion endotherm at 232°C which on calibration with pure tin was shown to correspond to 15 wt.% free tin in the $NbSn_2$ sample. This free tin was taken into account in the calculation of the overall Nb/Sn ratios used in the various powder mixtures.

The mixtures given in Table 2 were studied as these were either appropriate to the powder processing technique or corresponded to regions of the Nb–Sn phase diagram which required clarification.

Differential thermal analysis

A Stanton–Redcroft differential thermal analyser, model 673-h, was used in this study. Samples of mass 0.14–0.27 g were contained in silica crucibles, and calcined alumina powder (ICTA standard) was used as the reference

TABLE 1

Chemical analysis of powders

$NbSn_2$ (wt.%)	Ag	0.001	Si	0.01–0.1
	Co	0.001	Zr	0.005–0.05
	Fe	0.01–0.1	Ca	0.005–0.05
	Mo	0.001	Cu	0.001–0.01
	Sb	0.005–0.05	Mn	0.001
	V	0.001	Pb	0.005–0.05
	Al	0.01–0.1	Ti	0.01–0.1
	Cr	0.01–0.1	Ni	0.001
	Mg	0.01–0.1		
Nb (p.p.m.)	C	20	Ni	10
	N	40	Sb	10
	O	1660	Si	15
	H	5	Mo	10
	Ta	575	Zr	10
	Fe	55	Co	10
	Ca	10	Cu	20
	Pb	1	Mn	10
	W	100	Al	10
	Mg	10	As	5
	Ti	10	Te	5
	Cr	10	B	20
	V	10	Zn	10
	Sn	10	Bi	5

material in all experiments. A heating and cooling rate of 20°C min^{-1} was used in the thermal cycling. High purity argon, flow rate 250 ml min^{-1}, was used as the ambient atmosphere in order to prevent oxidation of the

TABLE 2

Summary of powder mixtures studied

	Nb (at.%)	Sn (at.%)
Nb–Sn powders	88.4	11.6
	75.0	25.0
	50.1	49.9
	40.2	59.8
	30.1	69.9
$Nb–NbSn_2$ powders	90.0	10.0
	79.8	20.2
	73.4	26.6
	55.1	44.9
	36.0	64.0
	28.6	71.4

specimens. After differential thermal analysis there was a slight reduction in sample weight (less than 2%) which was probably caused by the evaporation of tin. During the course of an experiment the samples were heated from room temperature to 1000°C and were then cycled between 1000°C and 650°C until constant, or almost constant, DTA traces were obtained. It was not anticipated that the production of constant DTA traces automatically meant that the equilibrium state had been reached for the mixture under study in view of the extremely sluggish nature of the types of reaction involved. However, the constant traces did indicate that reaction had effectively ceased as far as the thermal cycling was concerned.

X-Ray diffraction analysis

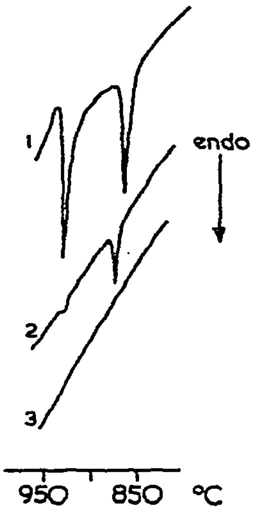
X-Ray diffraction analysis, using a Philips diffractometer and CuK_α radiation, was carried out after thermal analysis for a number of the samples in order to identify the phases that had been produced during the thermal cycling experiments.

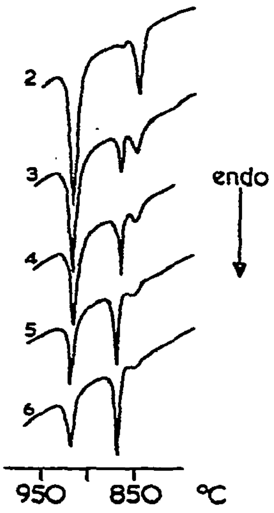
RESULTS

Differential thermal analysis

Representative differential thermal analysis traces for the various powder mixtures obtained on the heating cycle (650–1000°C) during repeated thermal cycling have been collected together for easy visual comparison in Figs. 1–11. At low temperatures the first thermal event that was observed for all the samples was the tin fusion endotherm at 232°C. This peak served as a low temperature calibration check for each new sample but disappeared for a number of samples after a few cycles as the free tin was consumed by reaction with the niobium. In the first heating of all the samples there were always a number of exothermic thermal events which occurred in the region 475–540°C. These peaks are associated with the reaction of the powders to form intermetallic compounds as diffusion interaction occurs. It is anticipated that this temperature range is not critical as far as the binary phase diagram is concerned, more likely, it simply represents the temperatures at which the Nb/$NbSn_2$ and Nb/Sn mixtures begin to react. Certain samples were cooled past this temperature region after the first heating cycle: however, these exotherms were never observed again. It appears, therefore, that the major amount of reaction occurs during the first heating cycle and this reaction is indicated by the exothermic peaks.

Following the tin fusion endotherm and the exothermic reaction peaks in the first thermal cycle, up to three endothermic peaks were observed during the heating stage of subsequent cycles between 650°C and 1000°C. On





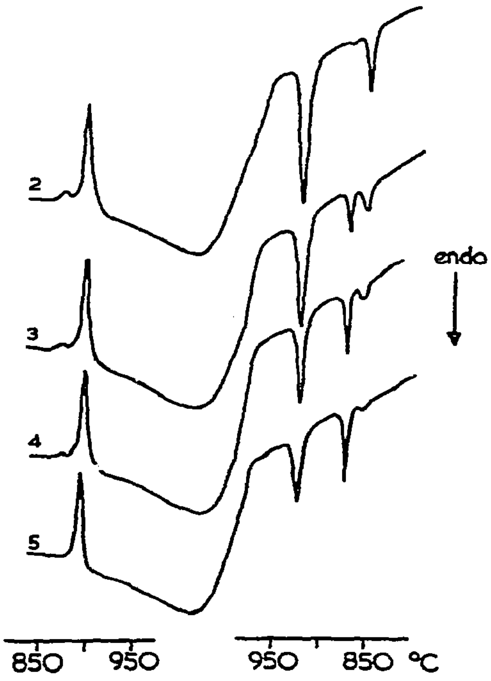
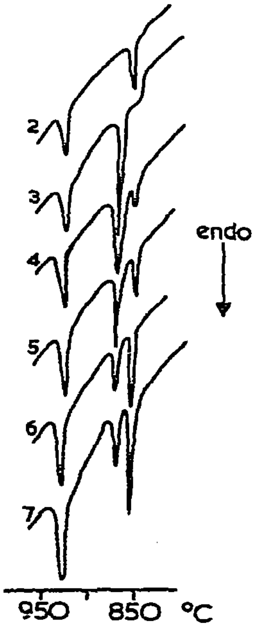
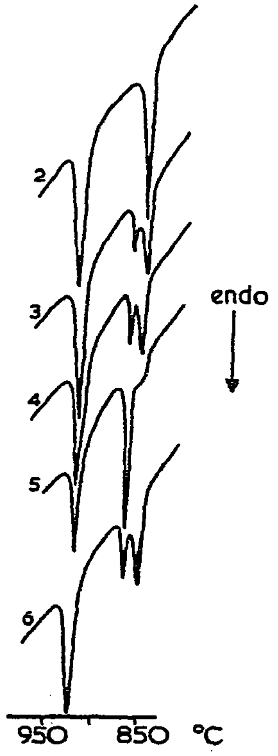


Fig. 1. DTA traces for Nb–11.6 at.% Sn mixture (heating).

Fig. 2. DTA traces for Nb–25 at.% Sn mixture (heating).

Fig. 3. DTA traces for second–fourth heating and cooling cycles for Nb–25 at.% Sn mixture.





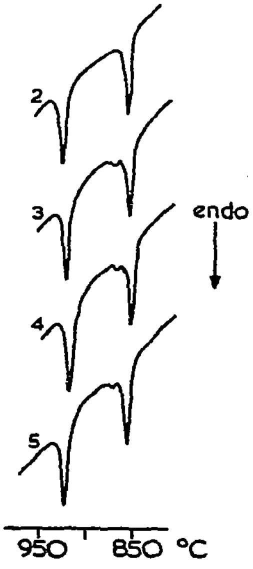
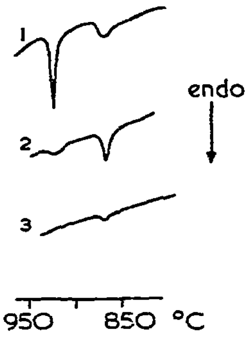
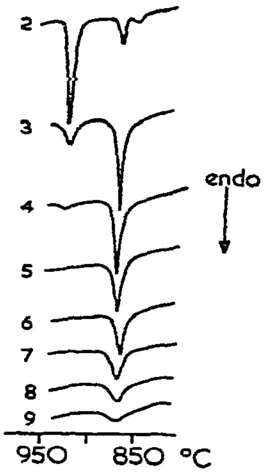


Fig. 4. DTA traces for Nb–49.9 at.% Sn mixture (heating).

Fig. 5. DTA traces for Nb–59.8 at.% Sn mixture (heating).

Fig. 6. DTA traces for Nb–69.6 at.% Sn mixture (heating).





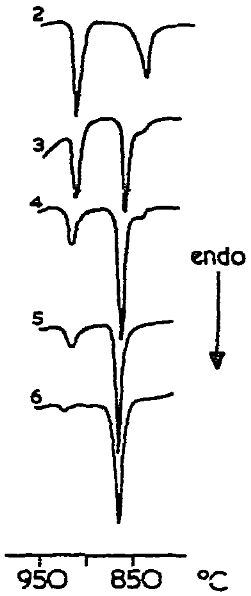
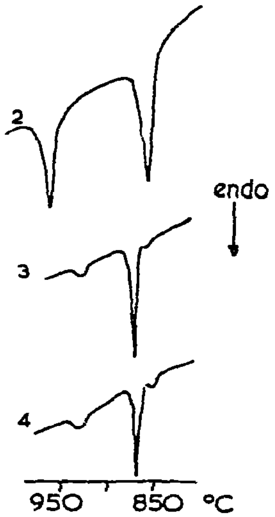


Fig. 7. DTA traces for Nb–$NbSn_2$ mixture containing 10 at.% Sn (heating).

Fig. 8. DTA traces for Nb–$NbSn_2$ mixture containing 20 at.% Sn (heating).

Fig. 9. DTA traces for Nb–$NbSn_2$ mixture containing 26.6 at.% Sn (heating).

occasions only two of the three peaks were present and the relative heights of the peaks altered between different samples and different stages in the thermal cycling process. Consecutive cycling in some cases caused the gradual disappearance and appearance of some of the peaks (see Figs. 1–11).



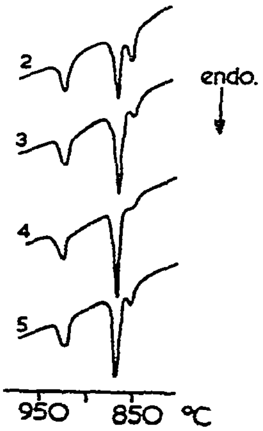


Fig. 10. DTA traces for "as-received" $NbSn_2$.

Fig. 11. DTA traces for Nb–$NbSn_2$ mixture containing 64 at.% Sn (heating).

The starting temperatures of the three peaks were fairly constant from sample to sample and from cycle to cycle for any given sample at temperatures of 845 ± 5°C, 865 ± 10°C and 930 ± 5°C.

During the cooling part of each cycle (1000°C–650°C) three exotherms corresponding to the three heating endotherms were never detected. The endotherm at 930°C was never matched by a corresponding exotherm on cooling. Of the other two endotherms neither was matched exactly at temperatures of 865°C or 845°C although two exotherms were seen on the cooling cycle. However, frequently only one exotherm at approximately 855°C was observed on cooling. Consequently, it is obvious that equilibrium conditions did not prevail in the cycling experiments, and that at least one extremely sluggish reverse reaction is by-passed during the cooling cycle.

At the completion of thermal cycling the samples were cooled to room temperature and a tin solidification exotherm at 232°C, which indicated the presence of unreacted tin, was observed in the "as-received" $NbSn_2$ sample, in the $NbSn_2$–Nb mixture containing 64 at.% Sn and in the Nb–Sn mixtures containing 69.9 at.% Sn, 59.8 at.% Sn and 49.9 at.% Sn. Residual tin was found in these samples because segregation, which occurred during cycling, had produced a tin-rich layer on the powder mixtures and had thus dramatically reduced the rate of reaction.

X-Ray diffraction analysis

X-Ray diffraction analysis of the "as-received" $NbSn_2$ sample confirmed the presence of $NbSn_2$ and a considerable proportion of free tin. After thermal cycling the $NbSn_2$ sample was shown to contain mainly tin and Nb_3Sn along with one or two minor lines that could be associated with $NbSn_2$. The Nb–$NbSn_2$ mixture containing 10 at.% Sn was shown to contain only Nb and Nb_3Sn after thermal cycling.

The Nb–Sn mixture with the lowest Sn content (11.6 at.% Sn) was found to contain only Nb_3Sn and Nb after cycling, whereas the mixture containing 49.9 at.% Sn contained Nb_3Sn, $NbSn_2$ and Sn after thermal analysis. No evidence of Nb_6Sn_5 was detected in this, or in any other sample after being cooled to room temperature. The elemental powder mixtures containing 59.8 at.% Sn and 69.9 at.% Sn were similarly found to contain free Sn, Nb_3Sn and $NbSn_2$.

DISCUSSION

There seems little doubt that the exotherms that occur on the first heating of each powder mixture are associated with the reaction of the powders to produce intermetallic compounds. Within the binary Nb–Sn system there are three accepted intermetallic compounds, namely $NbSn_2$, Nb_6Sn_5 and

Nb_3Sn. The structures of the phases are well established; however, certain disagreements exist with respect to their compositional ranges and thermal stabilities. The most likely reactions that could occur on heating the elemental powder mixtures are

$3\ Nb(c) + Sn(l) \rightarrow Nb_3Sn(c)$,

$Nb_3Sn(c) + 5\ Sn(l) \rightarrow 3\ NbSn_2(c)$

and

$Nb(c) + 2\ Sn(l) \rightarrow NbSn_2(c)$

Whilst in the $Nb/NbSn_2$ mixtures it seems that the reaction

$NbSn_2(c) + 5\ Nb(c) \rightarrow 2\ Nb_3Sn(c)$

is the most probable. Certainly the compound Nb_3Sn should be expected as a product phase as it is the most stable intermetallic phase in the binary system [14]. There is the possibility that the stoichiometries of the above reactions could be altered such that Nb_6Sn_5 is produced. However, although this compound is given a low temperature stability in the generally accepted binary phase diagrams of Ellis and Wilhelm [13], Van Vucht et al. [12] and Charlesworth et al. [11] (as shown in Fig. 12), there are other equally modern versions of the binary phase diagram that have been evolved in the U.S.S.R. by Kuznetsova et al. [10] (as shown in Fig. 13) and Svechnikov et al. [9] in which Nb_6Sn_5 is shown to be stable only within a very narrow temperature range above approximately 815°C. It is anticipated, however, that the compounds which are formed initially may not be too important because the thermal cycling over the temperature range 650–1000°C will cause phase changes to occur as various phase boundaries are traversed. Ideally the powder mixtures will continue to react during thermal cycling and hence

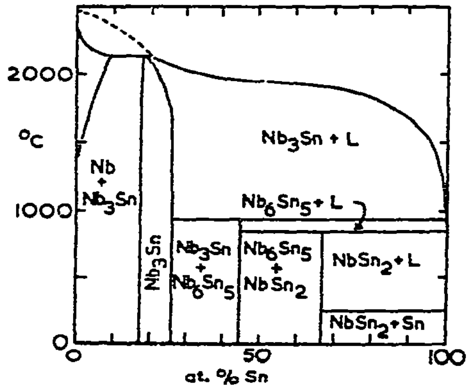


Fig. 12. Nb–Sn diagram according to Charlesworth et al. [11].

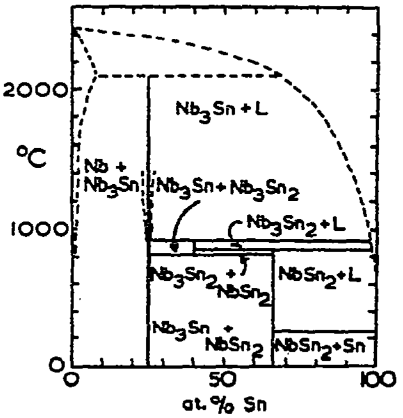


Fig. 13. Nb–Sn phase diagram according to Kuznetsova et al. [10].

approach the equilibrium phases for each individual mixture at which point constant differential thermal analysis traces may be expected to be produced. It remains, therefore, to attempt to explain the thermal traces given in Figs. 1–11 for the various heating cycles in terms of the existing phase diagrams and the possible phase changes that may occur as reaction takes place between the powders. However, it is important at this stage to reiterate that although three endothermic peaks were often seen on heating (845, 865 and 930°C) only peaks approximating to the former two of these were seen as corresponding exotherms on cooling and in many cases only one exotherm was visible. Consequently, it is apparent that equilibrium phase transformations did not occur during both the heating and cooling cycles.

Elemental powder mixtures

As indicated in the previous section, five elemental powder mixtures were investigated; namely, niobium with 11.6 at.% Sn, 25.0 at.% Sn, 49.9 at.% Sn, 59.8 at.% Sn and 69.9 at.% Sn, so that a wide range of compositions across the binary phase diagram was covered.

Figure 1 shows the thermal traces obtained for the mixture containing 11.6 at.% Sn. According to the binary phase diagrams of most investigators this composition is in the α-Nb plus Nb_3Sn two-phase field which, at this composition, extends to a temperature of approximately 2130°C. Consequently, it may be expected that the thermal cycling of an equilibrium mixture at this composition will produce a thermal analysis trace that consists of a flat baseline with no peaks. As can be seen from Fig. 1 this situation is reached by the third cycle. It is, however, interesting to note that before complete reaction has occurred in this mixture two peaks at approximately 842°C and 930°C are present on the DTA traces for the first and second cycles. These peaks indicate that the two-phase field existing on the tin-rich side of the diagram next to the single-phase Nb_3Sn region may contain another phase field with boundaries at these temperatures. The diagrams of Charlesworth et al. [11] (Fig. 12) and Van Vucht et al. [12] show a region containing Nb_3Sn and Nb_6Sn_5 next to the Nb_3Sn phase field, however, this region is shown to be stable up to a temperature of 930 ± 8°C, at which point Nb_3Sn and liquid are formed. The diagram of Kuznetsova et al. [10] (Fig. 13), which predicts a limited stability of an intermetallic phase intermediate between Nb_3Sn and $NbSn_2$ (designated Nb_3Sn_2) over the temperature range 820–910°C, gives a two-phase field containing Nb_3Sn and Nb_3Sn_2 which extends over the composition range from approximately 24 at.% Sn to 40 at.% Sn and over the temperature range 820–910°C. Consequently, although the temperatures do not agree exactly with those of the peaks shown in Fig. 1, this form of the phase diagram does indicate that two peaks may be expected in the 820–910°C region on heating a powder mixture containing Nb, Sn, Nb_3Sn and $NbSn_2$ within a partially-reacted mixture. Under such circumstances the Nb_3Sn and $NbSn_2$ mixture would be stable until approximately 820°C, at which point the boundary with the Nb_3Sn and Nb_6Sn_5 (Nb_3Sn_2 according to Kuznetsova et al.) phase field would be crossed. The new mixture Nb_3Sn and Nb_6Sn_5 would then be stable until a temperature of approximately 910°C is reached, at which point the Nb_3Sn plus liquid phase field is reached. The resultant DTA trace would, therefore, be expected to show two endothermic peaks. It is, however, important to emphasise that an equilibrium cooling cycle between the first and second cycles would also be expected to yield two peaks on a DTA trace as these two boundaries are crossed. However, as indicated earlier, the upper temperature peak at approximately 930°C was never seen in any of the cooling cycles and hence indicates that the peaks seen on heating may not all be related to equilibrium phase transformations which may be predicted from the phase diagram. This will be discussed more fully later in this section. At the end of the three heating cycles shown in Fig. 1, the 11.6 at.% Sn mixture was found by X-ray diffraction analysis to contain only α-Nb and Nb_3Sn and so it is apparent that it had reacted to give the equilibrium products in agreement with all the phase diagrams.

Typical DTA traces obtained on the thermal cycling of the mixture containing 25 at.% Sn are shown in Fig. 2. The equilibrium product on complete reaction of this mixture should be stoichiometric Nb_3Sn and so the DTA traces may be expected to follow the pattern outlined for the 11.6 at.% Sn mixture. However, from Fig. 2 it can be seen that the relatively simple behaviour of the 11.6 at.% Sn mixture is not repeated for the 25 at.% Sn sample. The DTA traces shown in Fig. 2 are more complicated in that a flat baseline, indicating complete reaction, is never obtained. In addition, the stage of incomplete reaction corresponding to the two peaks shown on the DTA traces for the 11.6 at.% Sn mixture is not achieved. A third peak at an intermediate temperature of 870°C, which increases in size with cycling, occurs on the DTA traces for the 25 at.% Sn mixture. The presence of three peaks may be explained by reference to the phase diagram of Kuznetsova et al. [10] if it is postulated that the state of incomplete reaction in the mixture corresponds to proportions of Nb_3Sn and $NbSn_2$ equivalent to the compositional range 40–67 at.% Sn. Under such circumstances cycling between 650 and 1000°C would cause the phase boundaries at approximately 820, 850 and 910°C to be crossed and hence cause the appearance of three peaks on the DTA trace.

Study of the diagram of Charlesworth et al. [11] leads to the prediction of two peaks on the DTA trace at 845 and 930°C for a mixture equivalent to a composition of 44–67 at.% Sn. In contrast, predictions based on the diagram of Svechnikov et al. [9] would indicate that four peaks may be expected on the DTA trace for mixtures having compositions within this range.

As for the 11.6 at.% Sn mixture the cooling cycles of the 25 at.% Sn mixture did not yield exotherms corresponding to the endotherms obtained on heating (as shown on Fig. 3 where it can be seen that only one major exotherm is present). Consequently, it is again apparent that the three endotherms obtained on heating may not all be related to equilibrium transformations indicated on phase diagrams.

Figures 4, 5 and 6 show the DTA traces obtained for the Nb–49.9 at.% Sn, Nb–59.8 at.% Sn and Nb–69.9 at.% Sn mixtures, respectively. There is no doubt that the last trace for each mixture does not correspond to the equilibrium product for that mixture because free tin was found in each sample at the end of thermal cycling. X-Ray diffraction analysis of all the samples at completion of cycling indicated only Nb_3Sn, $NbSn_2$ and free tin to be present.

It is again interesting to note that all mixtures produced evidence of endothermic peaks at approximately 845, 865 and 930°C on heating (in agreement with the traces obtained for the 25 at.% Sn mixture) but again produced only one or two peaks on the respective cooling cycles. Consequently, although it is tempting to use the phase diagram of Kuznetsova et al. [10] to explain the observations made on heating (and indeed the converse situation may be considered, i.e. the DTA traces could be used to construct a phase diagram similar to that of Kuznetsova et al.), such a treatment of the data would ignore the observations made on cooling. It is apparent, therefore, that the explanation of the DTA traces may require more than a simple comparison of peak temperatures with the published binary phase diagrams.

There is little doubt that at temperatures above 930–940°C the equilibrium phase for mixtures ranging from 26 at.% Sn to almost 100 at.% Sn are Nb_3Sn and a liquid of variable composition. On cooling, according to both Charlesworth et al. [11] and Kuznetsova et al. [10], an intermediate intermetallic phase between Nb_3Sn and $NbSn_2$ is produced peritectically from the Nb_3Sn and the liquid at a temperature of 910–940°C. This intermetallic phase is presently acknowledged as being Nb_6Sn_5. Such peritectic reactions are well known for the non-equilibrium nature of the products and their sluggish kinetics because they rely upon reaction of a solid phase with a liquid phase to produce a second solid phase. Consequently, this second solid phase inevitably forms as a peritectic sheath around the first reacting solid and so isolates the two reactants. Further reaction is slow as it requires diffusion through the peritectic product in order to obtain more product.

A second peritectic reaction between Nb_6Sn_5 and liquid to produce $NbSn_2$ is predicted by Charlesworth et al. [11] at 845 ± 7°C for compositions ranging from approximately 44 at.% Sn to 100 at.% Sn. Kuznetsova et al. [10] show a second peritectic reaction to produce $NbSn_2$ at compositions of 67 at.% Sn and above. It is not surprising, therefore, that the mixtures containing the high percentages of tin (which tend to segregate into two layers) do not produce equilibrium products and equilibrium thermal traces on cooling. It appears that the peritectic reaction that forms Nb_6Sn_5 is completely by-passed on cooling, with the result that Nb_3Sn and $NbSn_2$ are the only two intermetallic compounds found in the cooled solids. However, it is known from the results of the powder sintering experiments referred to in the introduction and from the results of other workers [11,12] that Nb_6Sn_5 can be produced at temperatures below 820°C (the lower temperature limit given for its stability by Kuznetsova et al.). Consequently, it appears that the various DTA traces may be explained in terms of the reaction of non-equilibrium Nb_3Sn and $NbSn_2$ on heating to produce Nb_6Sn_5. This reaction would be detected as the first endotherm. On further heating, the sequence of thermal events predicted from a diagram of the form given by Charlesworth et al. then occurs, namely, reaction of Nb_3Sn and Nb_6Sn_5 at approximately 930°C to give Nb_3Sn and liquid for compositions below 44 at.% Sn but above 26 at.% Sn, whilst for compositions between 44 at.% Sn and 67 at.% Sn the Nb_6Sn_5 and $NbSn_2$ yield Nb_6Sn_5 plus liquid at an intermediate temperature before producing Nb_3Sn plus liquid at 930°C.

Niobium–$NbSn_2$ powder mixtures

The DTA traces obtained for the various Nb–$NbSn_2$ powder mixtures are shown in Figs. 7–11. In general terms these mixtures produce the same form of DTA traces as the equivalent Nb–Sn powder mixtures. This is particularly so for the low % Sn compositions for which extensive segregation did not occur. Accordingly, the Nb–$NbSn_2$ mixtures of compositions 10 at.% Sn and 20 at.% Sn, which lie in the α-Nb plus Nb_3Sn region of the phase diagram, eventually produced DTA traces which show practically no peaks at all. As alloying proceeds the peaks evident in Figs. 7 and 8 become smaller and smaller as less $NbSn_2$ remains in the mixture. As for the elemental powder mixtures, the peak at approximately 865°C increased in size over the first few thermal cycles and was the last to disappear on repeated cycling. The Nb–$NbSn_2$ mixture containing 26.6 at.% Sn shows similar DTA traces to the 25 at.% Sn elemental mixture. Three peaks were again apparent and so the explanation postulated for the elemental powder mixture holds for the Nb–$NbSn_2$ mixture.

Figure 10 shows the DTA traces obtained on the thermal cycling of the "as-supplied" $NbSn_2$ powder, which contained 15 at.% free Sn. From any of the phase diagrams shown previously it may be expected that the cycling of this sample would produce a consistent set of traces showing peaks at the $NbSn_2$ plus liquid/Nb_6Sn_5 plus liquid boundary and at the Nb_6Sn_5 plus liquid/Nb_3Sn plus liquid boundary. However, the traces shown in Fig. 10 again show three peaks on heating although these were not repeated on cooling. X-Ray diffraction analysis of the products of cycling showed the presence of Nb_3Sn; $NbSn_2$ and Sn, with only traces of $NbSn_2$, which again proves the sluggish nature of the peritectic reactions that yield Nb_6Sn_5 and $NbSn_2$. Because of the sluggish nature of these reactions the thermal cycling has in effect brought about the decomposition of $NbSn_2$ to yield Nb_3Sn and Sn. A similar decomposition of $NbSn_2$ on heating has also been reported by Van Vucht et al. [12] during electrical resistance measurements of Nb–Sn powder samples made with a heating rate of 30°C min^{-1} and a cooling rate of 10°C min^{-1}. Consequently, on heating the non-equilibrium mixtures of Nb_3Sn, $NbSn_2$ and Sn that have been produced on cooling, the three peaks observed previously for such mixtures were again produced.

The Nb–$NbSn_2$ mixtures containing 64 at.% Sn produced similar traces to those obtained for the high at.% Sn elemental powder mixtures. Three peaks at 845, 865 and 930°C were again clearly visible and the sample was found to have segregated to give a tin-rich layer similar to those found in the elemental powder mixtures. It is apparent that decomposition of the $NbSn_2$ to give Nb_3Sn and Sn has again occurred because of the sluggish nature of the peritectic reactions that are required to produce the equilibrium $NbSn_2$ plus liquid mixture at 650°C from the Nb_3Sn plus liquid mixture at 1000°C.

CONCLUSIONS

The thermal cycling of Nb–Sn and Nb–$NbSn_2$ powder mixtures over the temperature range 650–1000°C at a rate of 20°C min^{-1} does not produce the thermodynamically equilibrium products (except in the case of low tin contents of 10 at.% Sn) because of the extremely sluggish kinetics of the various peritectic reactions involved in the cooling cycles and because of the segregation of tin.

On thermal cycling over the temperature range 650–1000°C, $NbSn_2$ decomposes into Nb_3Sn and Sn because of the extremely sluggish nature of the peritectic reactions required to produce Nb_6Sn_5 and $NbSn_2$.

Many of the mixtures that have been investigated produced three peaks on the DTA traces on heating in the temperature range 840–930°C. The interpretation of these data may be made in terms of the reaction of metastable Nb_3Sn, $NbSn_2$ and Sn, which have been retained on cooling because of the slow kinetics of the peritectic reaction involved in the formation of Nb_6Sn_5, followed by a sequence of phase changes in accordance with the form of the phase diagram of Charlesworth et al. [11]. However, an alternative explanation of the curves may be made in terms of the phase diagram given by Kuznetsova et al. [10], although such an explanation would not easily explain the forms of the DTA traces observed on cooling the samples. Consequently, the DTA data illustrate very well the dangers inherent in the use of this technique alone for the determination of equilibrium phase diagrams of alloy systems involving peritectic reactions.

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