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MÖSSBAUER SPECTROSCOPY OF LANTHANON–TIN AND IRON–TIN PHASES AND THEIR REACTION PRODUCTS WITH CARBON AND NITROGEN

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Abstract—Mössbauer parameters have been obtained at 80°K for a number of lanthanon–tin and iron–tin phases, including Ce_3Sn, Ce_2Sn, Ce_2Sn_3, $CeSn_3$, Pr_3Sn and Fe_3Sn. These data have been used in conjunction with other studies to help clarify the phase relationships in the Ln–Sn systems. Reaction of substoichiometric quantities of carbon with the binary alloys Ce_3Sn and Pr_3Sn and the mixed phases of composition La_3Sn and Ho_3Sn gave single-phase products Ln_3SnC_x ($x \leq 0{\cdot}66$); with excess carbon, complete decomposition to Ln_2C_3 and Sn occurred. By contrast Ln_3Sn reacted with excess of nitrogen to give LnN and $LnSn_3$; with limited nitrogen a cubic ternary phase Ln_2SnN_x appears to be formed. Further information on bonding has come from a comparison of the ^{57}Fe and ^{119}Sn Mössbauer spectra of Fe_3Sn and Fe_3SnC.

INTRODUCTION

THE EXISTENCE of lower carbides of the lighter lanthanon elements has been the subject of recent work[1]. To further these studies work was undertaken to prepare and study lanthanon–tin carbides[2]. An important part of the work has been the determination of the Mössbauer parameters of the tin nuclei in these materials, with the aims of studying the nature of the bonding in the alloys and carbides and of testing the hypothesis of strong atomic interactions between tin and lanthanons. This latter hypothesis is suggested by the high melting points of these compounds[3]. Preliminary work on the reaction of nitrogen with the alloys has also been facilitated by the use of the Mössbauer technique. When heated with an excess of nitrogen at moderate temperatures the disproportionation of cubic Ln_3Sn leads to very small crystallites at the limit of X-ray detection, which results in very poor X-ray films which are not easy to interpret. On the other hand, Mössbauer spectra were obtained and interpreted relatively quickly and easily.

The fact that the chemical isomer shift of the tin atom in Ln_3SnC_x shows no significant change from that in the Ln_3Sn alloys suggests that the carbon has very little effect on the bonding of the tin, while strong lanthanon metal–carbon bonding in these materials has been demonstrated by hydrolysis and other studies[2]. Further confirmation of strong Ln–C interactions was desirable, but since this

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1. J. S. Anderson, N. J. Clark and I. J. McColm, *J. inorg. nucl. Chem.* **31**, 1621 (1969).
2. I. J. McColm, B. Mortimer and N. J. Clark, *J. inorg. nucl. Chem.* **33**, 49 (1971).
3. A. Percheron and J. C. Mathieu, *Proc. 7th Rare Earth Res. Conf.* 221 (1968).

could not be directly investigated at the time experiments with Fe_3Sn and Fe_3SnC_x were undertaken to elucidate the nature of electron transfer processes in these systems.

EXPERIMENTAL

The materials were made by melting high purity (> 99·9%) reagents under purified dried argon on apparatus previously described[2]. Some of the preparations were examined immediately; others were annealed for up to 10 d. in evacuated silica ampoules at 950°C.

The reaction of the alloys with nitrogen was studied on a Stanton Mass Flow thermal balance using oxygen-free nitrogen at temperatures up to 1050°C. Another procedure was used for the specimens of low nitrogen content whereby pieces of the alloys were sealed under dry nitrogen in small silica ampoules.

Samples were characterised by X-ray powder methods using an 11·46 cm Debye-Scherrer camera with Co or CrK_α radiation. Metallographic examination of specimens polished and then etched with nital under dry argon was also carried out. The methods used for chemical analysis have been described previously[2].

Mössbauer spectra were recorded at room temperature or at 80 K using techniques described in a previous paper[4], but with a spectrometer incorporating an R.I.D.L. multichannel analyser. The iron source was $^{57}Co/Pd$ and the tin source was ^{119}Sn in the form of Pd_3Sn; these gave experimental line widths of the order of 0·25 and 0·8 mm s^{-1} respectively, for single-line absorbers. Data were analysed by computer methods[5], and in cases where a broad unresolved line was observed, it was fitted with a single Lorentzian peak to obtain a least-squares estimate of the centroid. The chemical isomer shifts are probably accurate to within ±0·05 mm s^{-1}.

RESULTS AND DISCUSSION

Binary alloys

Repeated attempts to prepare alloys with composition Ln_3Sn resulted in only two preparations worthy of further investigation, namely Ce_3Sn and Pr_3Sn. The intermetallic compound Ce_3Sn was shown to be single phase by X-ray and metallographic examination, while metallography revealed that the Pr_3Sn contained < 5% of a eutectic grain boundary material. The existence of these two phases has not been clearly demonstrated before, but the lattice parameter of the f.c.c. phase Pr_3Sn agrees with that of a phase reported by Nowotny[6] as part of a mixed product of this composition. The lattice parameter reported by Nowotny for Ce_3Sn does not agree with that found here, but in this work the metallographic examination showed a single-phase preparation with no eutectic, whereas Nowotny reported the material as being present in a eutectic mixture. Since no other single-phase or predominantly single-phase alloy of composition Ln_3Sn could be prepared, Mössbauer spectra were only obtained for Pr_3Sn and Ce_3Sn. Results in Table 1 show that the ^{119}Sn chemical isomer shifts, (δ), were the same within experimental error. The lines were very broad, due to unresolved quadrupole splitting and possible shift variations. One specimen of Pr_3Sn was annealed under vacuum for 160 hr at 950°C, and while no change in δ was detected the half-width of the line did decrease significantly. This suggests that there was less disorder in this specimen, but X-ray methods did not reveal any superstructure lines. Extremely long annealing times might eventually produce a completely-ordered structure.

Metallographic examination of compositions across the binary Ce–Sn system

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[4] T. C. Gibb, R. Greatrex, N. N. Greenwood and D. T. Thompson, *J. chem. Soc.* A, 1663 (1967).

[5] B. J. Duke and T. B. Gibb, *J. chem. Soc.* A, 1478 (1967).

[6] H. Nowotny, *Proc. 7th Rare Earth Res. Conf.* 309 (1968).

gave direct evidence for single-phase materials of composition Ce$_3$Sn, Ce$_2$Sn, Ce$_2$Sn$_3$ and CeSN$_3$. One typical micrograph is shown in Fig. 2. The X-ray data for Ce$_2$Sn and Ce$_2$Sn$_3$ were complicated and have not been completely indexed. Ce$_3$Sn and CeSn$_3$ were both f.c.c. Mössbauer data for these alloys are summarized in Table 1. A decrease in the tin content causes a fall in the chemical isomer shift, which probably reflects an increased tendency of the tin to donate electrons to the *f* band of cerium.

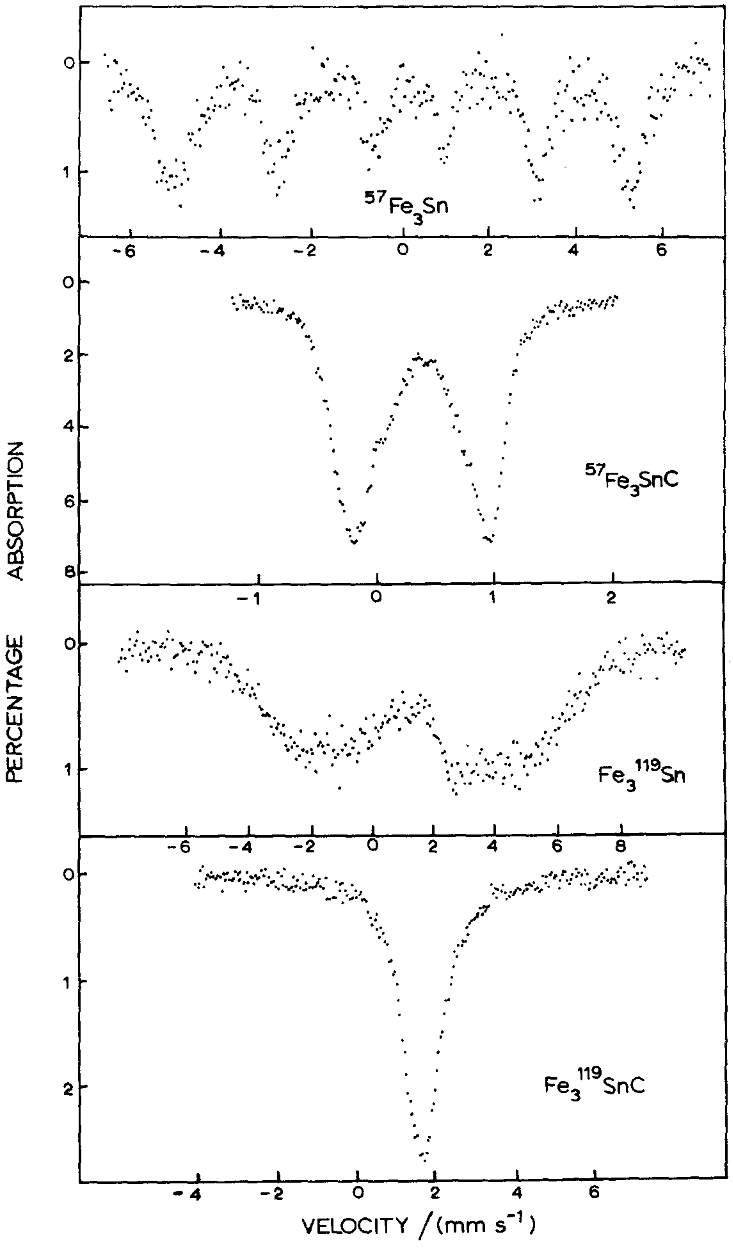

Fig. 1. Iron and tin Mössbauer spectra of Fe$_3$Sn and Fe$_3$SnC.

Table 1

Compound	Chemical isomer shift δ (mm s^{-1}) *	Quadrupole splitting (mm s^{-1}) *	Line half width (mm s^{-1}) *
Ce_3Sn	+2·04	Q	1·74
Pr_3Sn Arc-melted	+1·99	Q	1·87
Pr_3Sn Long-annealed specimen	+2·02	Q	1·56
Ce_3Sn	+2·04	Q	1·74
Ce_2Sn	+2·00	Q	1·79
Ce_2Sn_3	+2·45	Q	1·83
$CeSn_3$	+2·59	1·13	1·13, 1·11
$PrSn_3$†	+2·50	1·10	
$NdSn_3$†	+2·49	1·11	
$SmSn_3$†	+2·54	1·05 (1·11 at 4·2°K)	

† From Ref. [7].

*All data at 80 K. δ with respect to SnO_2 at 295 K.

Q signifies broadened resonance line.

The relatively sharp lines in the spectrum of $CeSn_3$ provide a clearly quadrupole-split spectrum and argue for considerably more order in this alloy than in the other phases in this system. Ordering in $CeSn_3$, with Sn atoms at the face centres of the cubic unit cell, gives a tin site with an axially-symmetrical electric field gradient which would produce the quadrupole splitting. The parameters found here for $CeSn_3$ are in accord with the values given by Borsa[7] for $PrSn_3$, $SmSn_3$ and $NdSn_3$. Table 1 shows that the parameters are very similar and independent of the lanthanon. These data do not agree with earlier work[8] which shows considerable variation in δ depending upon the lanthanon used to form $LnSn_3$. Kanekar[8] also reported that the splitting increased considerably at low temperatures. The results for $CeSn_3$ support Borsa's findings and not the earlier ones.

Carbide phases

The reaction of carbon with the binary alloys Ce_3Sn and Pr_3Sn, with the mixed phases of composition La_3Sn, and with Ho_3Sn over a range of temperatures, showed that single-phase products Ln_3SnC_x could be obtained with $x <$ 0·66. This is also true for very high temperature reactions in the arc furnace. In all cases when x exceeded 0·66. X-ray examination revealed the presence of LnC_2 and Ln_2C_3 together with the f.c.c phase and some extra lines. The Mössbauer data in these cases showed that the Ln_3SnC_x phase still persisted.

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7. P. Borsa, R. C. Barnes, R. A. Reese, *Phys. Stat. Solidi* **19**, 359 (1967).
8. C. R. Kanekar, V. U. S. Rao, K. R. P. M. Rao, *Discussions of Conf. on Nuclear Interactions*, New Zealand (1966).

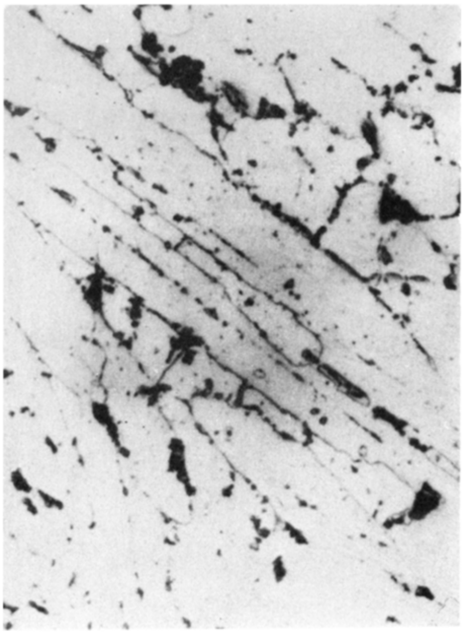

Fig. 2. Microstructure of Ce_2Sn_3 (×400) etched with nital.

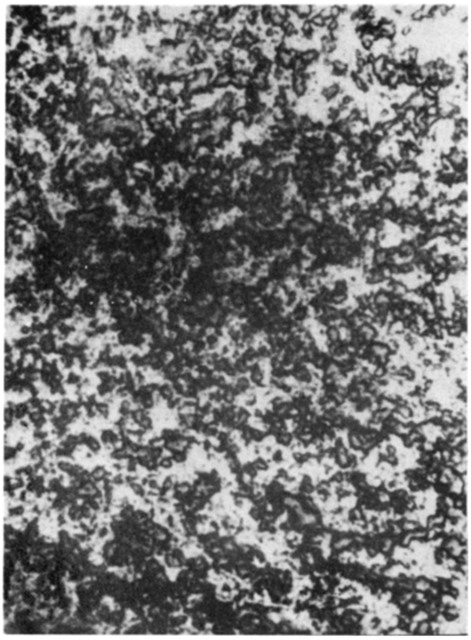

Fig. 3. Microstructure of the reaction product from Ce_2Sn and nitrogen at 900°C (×400) etched with nital. The light etching phase is $CeSn_3$.

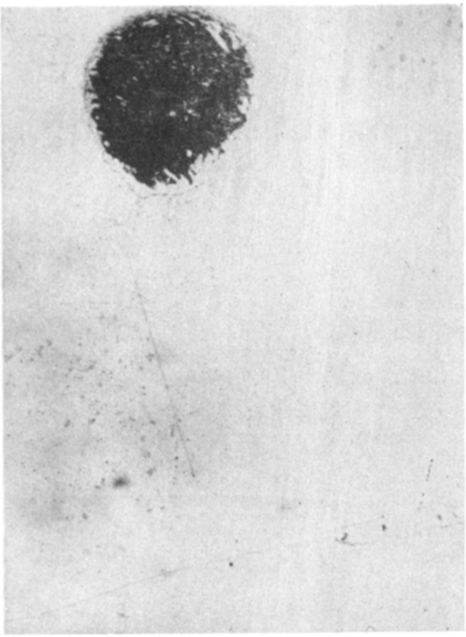

Fig. 4. Microstructure of annealed Fe_3Sn (×400) etched with nital.

As the data in Table 2 show, all the carbides have basically the same value of δ as Ce_3Sn with no noticeable effect on increasing the carbon content; this suggests that the carbon has very little effect on the bonding of the tin in these compounds. Once again the samples gave broad-lined spectra which can be attributed to gross disorder in the lattice causing variations in the tin environment. The great stability, relative to the binary lanthanide carbides, with respect to hydrolysis under mild conditions suggests considerable covalent character in the Ln–C bond[2]. While this has not been directly tested by the Mössbauer technique the results described below for Fe_3SnC_x show that the electronic structure of iron alters drastically on formation of the carbides.

Table 2 (all data at 80°K)

Compound	Chemical isomer* shift, δ (mm s^{-1})	Line width (mm s^{-1})
$Ce_3SnC_{0\cdot20}$	+2·04	1·87
$Ce_3SnC_{0\cdot61}$	+1·96	1·22
$Ce_3SnC_{1\cdot05}$†	+2·00	1·20
$Ce_3SnC_{1\cdot97}$†	+2·04	1·74
$Pr_3SnC_{0\cdot4}$	+1·98	1·56
$Pr_3SnC_{0\cdot32}$	+1·98	1·82
$La_3SnC_{0\cdot51}$	+2·02	1·22
$Ho_3SnC_{0\cdot48}$	+1·97	1·83

†Not a single phase; contained CeC_2.
*Relative to SnO_2 at 295°K.

In the presence of excess carbon even at low temperatures (900–1200°C) complete decomposition to Ln_2C_3 and Sn occurred if the reaction time was sufficiently protracted. This is in marked contrast to the reaction of the Ln_3Sn phase with excess nitrogen as discussed below.

Nitride phases

Below 580°C Ce_3Sn was unaffected by dry nitrogen, but at 600° a gain in weight registered on the thermal balance indicated incipient reaction; at 620°C a very rapid reaction was observed, with an eventual gain in weight corresponding to an overall composition of $Ce_3SnN_{2\cdot6}$. The product was porous, hard to handle, and very easily oxidised. It produced extremely poor X-ray films. However, a Mössbauer spectrum showed only one type of tin site giving a resonance line at 2·58 mm s^{-1} with a quadrupole splitting of 1·10 mm s^{-1} which corresponds to Sn in $CeSn_3$. The gain in weight on nitridation would then correspond to that predicted by Eq. (1).

$$3\,Ce_3Sn + 4\,N_2 \longrightarrow 8\,CeN + CeSn_3. \qquad (1)$$

This decomposition was confirmed by vacuum annealing the product prior to an X-ray determination, which then showed a very strong f.c.c. phase ($a =$

5·023 Å) and a weak f.c.c. phase ($a = 4·723$ Å) which agree with reported data for CeN ($a = 5·027$ Å) and $CeSn_3$ ($a = 4·724$ Å).

With Pr_3Sn no reaction occurred below 660°, but at 720°C a rapid gain in weight was observed. The overall composition after reaction ceased was $Pr_3SnN_{2·63}$, which again is in accord with the reaction shown in Eq. (1), which requires an overall product composition of $Pr_3SnN_{2·67}$. Mössbauer examination confirmed the presence of $PrSn_3$ and also showed that when a multiphase alloy of gross composition Sm_3Sn was treated in the same way all the tin is converted to the $SmSn_3$ phase. Data for these reactions are given in Table 3.

Table 3 (all data at 80°K)

Compound	Chemical isomer* shift, δ (mm s^{-1})	Quadrupole splitting Δ (mm s^{-1})	Line width (mm s^{-1})
$Ce_3SnN_{1·04}$	+2·07	Q	1·70
$Ce_3SnN_{2·04}$	+2·58	1·10	1·13, 0·88
$Pr_3SnN_{0·86}$	+2·00	Q	2·44
$Pr_3SnN_{2·66}$	+2·59	Q	1·68
Sm_3SnN	+2·62	Q	2·14

Q signifies broadened by quadrupole splitting and/or shift variation but not resolved.
*Relative to SnO_2 at 295°K.

The Mössbauer results from alloys heated in the presence of limited amounts of nitrogen are helpful in defining the course of the reaction. A mixture of Ce_3Sn and nitrogen with overall composition $Ce_3SnN_{1·06}$ was heated for 7 d at 950°C, but despite this long annealing time the X-ray film was of very poor quality. Two f.c.c. patterns could just be discerned with $a = 5·12$ Å and $a = 5·02$ Å. Metallography showed a grey matrix with a dispersion of a fine white globular material. The 5·02 Å phase is probably CeN, because the Mössbauer spectrum shows only one tin resonance which had the same broad spectrum as Ce_3Sn or Ce_2Sn. This suggests that under these conditions there is no dissociation into Ce and $CeSn_3$. The Mössbauer, X-ray and analytical data suggest that the 5·12 Å phase might be Ce_2SnN_x in equilibrium with CeN. A repeat experiment with overall composition $Ce_3SnN_{0·94}$ showed two phases present with $a = 5·02$ Å and $a = 5·11$ Å, but again only broad tin resonance corresponding to that in Ce_3Sn or Ce_2Sn.

A further decrease in the stoichiometric amount of nitrogen, but this time in the system $Pr_3SnN_{0·86}$, produced very inconclusive X-ray data from which it was too difficult to derive any lattice parameters. The broad Mössbauer peak was not shifted with respect to Pr_3Sn or Pr_2Sn and no other tin species were detected. Preparations with overall compositions $Ce_3SnN_{0·1}$, $Ce_3SnN_{0·3}$ and $Ce_3SnN_{0·5}$ were examined and again produced very poor X-ray films which were obviously more complex than f.c.c. patterns. In each case an f.c.c. phase was present with $a = 5·02$ Å and the other lines could arise from a somewhat expanded Ce_2Sn structure. This indicates that reaction of the Ln_3Sn phase with nitrogen proceeds via precipitation of CeN and Ce_2Sn. A subsequent experiment on the thermal balance showed that Ce_2Sn reacted readily with nitrogen in the temperature range 660–750°C to produce CeN and $CeSn_3$. Both these phases were confirmed by X-ray and metallography (Fig. 3) and the presence of $CeSn_3$ as the only tin-containing species was demonstrated by the Mössbauer technique. There is from this an indication that a cubic Ln_3SnN nitride does not exist, but rather a cubic phase Ln_2SnN_x. At present there is some uncertainty concerning the Ln_3SnN phase, for little work has been reported. Some work concerning Nd_3MN phases (M = Al, Ga, In, Tl, Sn and Pb) has been reported[6] where NdN and the B element were heated at 900°C for 5 days. The specimens were not homogeneous, but each had as a major phase an f.c.c. product. Lattice parameters for these phases are shown in Table 4 together with the reported values for the corresponding carbide. It is noteworthy that for the Al, Ga, In and Tl compounds the nitride cell is smaller than the carbide, while the reverse is true for the Sn and Pb compounds. The data obtained here and also shown in Table 4 show that the above reversal is true for the Ce_3Sn system.

In the neodymium case the reversal has been tentatively explained by Sn/Nd and Pb/Nd substitution occurring in the nitride but not the carbide. The Mössbauer work has shown here that in the Ce_3Sn and Pr_3Sn cases there is considerable disorder in the alloys, the nitrides and carbides, which does not allow one to resort to the above explanation. In fact it seems that in the Sn and Pb systems lattice disorder is a regular and necessary occurrence[2]. The work on the Nd_3MN systems has shown that ordering of the metallic parent lattice can easily be detected for Nd_3AlN_x. In fact ordering seems to be associated with carbides and nitrides of this type when the B metal is capable of forming a binary nitride or carbide[2, 13]. Carbon will form a ternary cubic carbide with Ln_3Sn alloys but it seems doubtful if nitrogen will form the corresponding nitride. The increased lattice parameter of the nitrides of Ce_3Sn, Nd_3Sn and Nd_3Pb compared to the respective carbides could be explained if these phases were actually M_2SnN_x.

Table 4. Lattice parameters (Å) of some cubic phases

	Al	Ga	In	Tl	Sn	Pb
Nd_3M*			4·94	4·934		
Nd_3MC*	4·96	5·136	5·045	5·042	5·029	5·05
Nd_3MN*	4·910	5·063	4·949	4·957	5·057	5·067
Ce_3M					5·04	
$Ce_3SnC_{0\cdot46}$					5·09	
$Ce_3SnN_{1\cdot06}$†					5·12	
$Ce_3SnN_{0\cdot96}$†					5·11	
Pr_3M					4·974	
$Pr_3SnC_{0\cdot32}$					5·023	

*Ref.[6].

†Two-phase material one of which is CeN.

The relatively short Ln–C distances in these cubic carbides indicates a strong interaction of the lanthanon and the non-metal, with some transfer of electrons from the non-metal filling the $4f$ band of the lanthanon metal atoms. There are no conclusive experiments to date which indicate a charge distribution in this way but in an attempt to gain some insight into this problem the system Fe_3SnC_x was investigated since the Mössbauer spectrum of Fe as well as Sn can be monitored.

The alloys Fe_3Sn *and* Fe_3SnC

There is some confusion concerning which intermetallic compounds exist in the binary Fe–Sn system above 50 atom% Fe[9, 10] but the equilibrium diagram indicates that an alloy of composition Fe_3Sn at room temperature would be a mixture of α Fe(Sn) and FeSn. For this reason all preparations were done on the arc furnace or a high-temperature tantalum furnace so that the small specimens used were rapidly cooled. This produced typical as cast structures with dendritic formation and very poor X-ray films. Some specimens were annealed above 830°C and rapidly cooled from this temperature. This gave a material with the microstructure shown in Fig. 4, with a white large grained matrix with isolated dark etching spheroids within. The spheroids appear to be eutectic in form, with a diffusion band at the grain boundary with the matrix. Examination of a number of micrographs shows that the matrix constitutes 90–95 per cent of the product. This material was used for the Mössbauer work and gave the data in Table 5 and Fig. 4, which show that neither Fe nor FeSn are present. The X-ray data were ambiguous because the Fe_3Sn phase previously described[10] could not be recognized and neither could FeSn be identified. Nevertheless, it is felt that the Mössbauer data and metallography confirm the presence of Fe_3Sn as a distinct phase. It will be noted that the hyperfine magnetic field is 317 kG at the iron nucleus and 70 kG at the tin nucleus.

The product obtained by reacting Fe_3Sn with carbon was shown unambiguously by X-ray diffraction to be the simple cubic phase previously identified by Stadelmaier as Fe_3SnC[11]. There is a marked increase in δ for iron on carbide formation which is widely interpreted in such systems as indicating a large

Table 5

		Fe_3Sn	Fe_3SnC
^{57}Fe	δ (mm s^{-1})*	+0·09	+0·35
	(mm s^{-1})	0	2·95
	H kG	317	0
	(mm s^{-1})		1·35, 1·14
^{119}Sn	δ (mm s^{-1})†	+1·54	+1·62
	H kG	70	0
	(mm s^{-1})		1·5

*Relative to iron metal at 295°K.
†Relative to SnO_2 at 295°K.

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9. M. Hansen, *Constitution of Binary Alloys* p. 719. McGraw-Hill, New York (1958).
10. O. Nial, *Ark. Kemi Mineral Geol.* **17B** (1943).
11. H. H. Stadelmaier and L. J. Huetter, *Acta Met.* 7, 415 (1959).

increase in the electron population of the 3 *d* band[12]. The complete destruction of the spin ordering in the iron even down to 80°K (see Fig. 1) confirms that the iron electron structure has altered drastically. The hyperfine magnetic field induced at the tin atom in Fe_3Sn also disappears in Fe_3SnC. The apparently large change in the δ value for tin in going from Fe_3Sn to Fe_3SnC may not be significant, as the magnetic spectrum is very badly broadened and makes accurate measurement of the chemical isomer shift difficult.

An increase in the population of the iron 3*d* band on carbiding the alloy is in line with donation of electrons from carbon to iron in this system. In the absence of other evidence it might be surmised that a similar transfer of electrons occurs from carbon to the 4*f* band of the lanthanon in the ternary phases Ln_3SnC_x.

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