JOURNAL OF MATERIALS SCIENCE 11 (1976) 836–842

A systematic investigation of the Mössbauer parameters of some intermetallic compounds and electroplated alloys of tin

J. SILVER
Crystal Growth Laboratory, Imperial College, London, UK
C. A. MACKAY
Tin Research Institute, Greenford, Middlesex, UK
J. D. DONALDSON
Department of Chemistry, Chelsea College, London, UK

The Mössbauer parameters of specific intermetallic binary compounds of tin are reported, together with those of electroplated tin-nickel, tin-copper and tin-cobalt alloys. These are interpreted on the basis of the band theory previously proposed (*et al.,* [24]). In addition a tentative correlation between the observed parameters and the known properties of electroplates is proposed.

1. Introduction

Although the ^{119}Sn Mössbauer parameters of a number of binary tin-containing alloys have been reported, no systematic studies of intermetallic and related compounds have been made [1-5]. Indeed reports of studies of such compounds in common with all metallurgical Mössbauer studies, often do not distinquish between results from solid solutions, eutectics, eutectoids or intermetallic compounds. Sometimes little detail is given about conditions under which samples are prepared and details of any heat-treatment which may have been given are omitted as is any metallographic description. Yet such details have a critical bearing upon the phases present in a sample when it is examined.

There seems a tacit assumption that such details are Mössbauer independent and that the net Mössbauer active element percentage is the crucial factor. This surely cannot be the case, a quick survey of the structure changes and density changes across even a moderately complex binary system must indicate essential bonding differences and with these discrete changes in S-electron density and hence discrete changes in the Mössbauer spectra. When two or more phases are present the net Mössbauer spectrum must be some combination of the responses from each phase, and very few reports attempt to separate the spectum due to each component.

In this work we have, in the main, isolated intermetallic compounds from samples prepared, where possible, in a liquid plus intermetallic compound phase region on the tin-rich side of the phase diagram. The tin-rich solid solution matrix being removed by dissolution in either Clarkes solution or a solution of caustic soda and ortho nitrophenol. In the case of Ni_3Sn and SbSn samples were cast in the single phase region and annealed until the X-ray diffraction patterns became sharp with readily resolvable high angle α_1, α_2 doublets. Electroplated coatings were simply stripped-off thin copper panels.

We now report the results of such an investigation relating the Mössbauer chemical shifts (δ) to the likely electron populations of conduction bands in these intermetallic compounds. The materials studied were selected to include tin in a range of chemical environments.

The Mössbauer parameters are also discussed in relation to the known environments of the tin atoms in intermetallic compounds and comments are made on possible tin environments for electroplated alloys, the structures of which, are not

TABLE I Mössbauer parameters for binary tin–alloy intermetallic compound (this work)

	Compound	Chemical Shift δ (mm sec^{-1}) ± 0.03 (rel. to $BaSnO_3$)	Quad split Δ (mm sec^{-1}) ± 0.03	Line width Π (mm sec^{-1}) ± 0.05	Temperature
(1)	α-Sn	2.05	–	–	N_2
(2)	β-Sn	2.50		1.46	N_2
		2.41		0.90	RT
(3)	Ni_3Sn	1.44		1.17	N_2
		1.52		1.11	RT
(4)	Ni_3Sn_2	1.63	1.36		N_2
		1.76	1.26		RT
(5)	Ni_3Sn_4	1.89	1.21		N_2
		1.91	1.16		RT
(6)	Ni–Sn Electroplate				
	plated at 0.5 A dec^{-2}	2.03	1.09		RT
	plated at 1.25 A dec^{-2}	1.89	1.22		N_2
		1.89	1.12		RT
	plated at 2.5 A dec^{-2}	1.91	1.09		RT
(7)	Cu–Sn elec.	2.02	1.32		N_2
		2.01	1.11		RT
(8)	Cu_3Sn	1.76		1.02	N_2
		1.71		0.91	RT
(9)	Cu_6Sn_5	2.26		1.81	N_2
		2.22		1.74	RT
(10)	Cu–Sn elec.	2.01		1.91	N_2
		2.01		1.91	RT
(11)	Ag_3Sn	2.14		1.10	N_2
		2.10		0.82	RT
(12)	SnSb: 53% Sn	2.69		1.22	N_2
		2.66		1.10	RT
	5% Sn	2.71		1.15	N_2
		2.66		0.90	RT
	48% Sn	2.69		1.21	N_2
		2.69		1.13	RT
	43% Sn	2.72		1.31	N_2
		2.74		1.11	RT
(13)	SnS	3.29	0.93		N_2
		3.26	0.86		RT
(14)	SnSe	3.30	0.83		N_2
		3.32	0.73		RT
(15)	SnTe	3.45		1.30	N_2
		3.42		0.93	RT
(16)	SnSe high temp. quick frozen	3.36		1.30	N_2
(17)	SnI_2	3.90			N_2

N_2 = liquid nitrogen temperature = – 196° C
RT = room temperature = 20° C

those of the equilibrium alloy of the same composition as indicated by the phase diagram.

2. Results and discussion

The Mössbauer parameters for the intermetallic compounds studied in this work are given in Table I and can be compared with data from previous studies, Table II. From the results in Tables I and II, it would seem that binary tin alloys with the transition metals of the first row, the later transition metals of 1st and succeeding rows, and the p-block elements, have chemical shift values in the ranges 1.4 to 2.26 mm sec^{-1}, 1.7 to 2.45 mm sec^{-1} and 2.4 to 3.24 mm sec^{-1} respectively.

Many authors [1, 5] have suggested that in various binary tin alloys electrons from the tin atoms contribute to the conduction bands in proportion to both the percentage of tin present and

TABLE II Published data of Mössbauer parameters for binary tin alloys

Elemental addition	Alloy composition % Al–Sn	Phase field	Chemical shift (mm sec^{-1}) (Rel. to BaSnO$_3$)	Reference
Pd	0–16%	Tin s.s.	1.41	[1]
	25%	Pd_3Sn	1.67	[1]
	33%	Pd_2Sn	1.56	[1]
	50%	PdSn	1.93	[1]
	66%	$PdSn_2$	2.18	[1]
	80%	$PdSn_4$	2.39	[1]
In	0–5%	Tin s.s.	2.45–2.48	[2]
	5–10%	Tin + γ	2.48–2.505	[2]
	10–25%	γ compound	2.505	[2]
	25–58%	$\beta + \gamma$	2.505–2.58	[2]
	58–72%	$\beta + \gamma$	2.58–2.85	[2]
	72–90	β compound	2.85	[2]
	94–100	Indium s.s.	2.835	[2]
Tl	0–56%	Tin s.s. + Thalium s.s.	2.45–2.53	[2]
	56–85%	Tin s.s. + Thalium s.s.	2.53–2.89	[2]
	85–100%	Thalium s.s.	2.89	[2]
Pb	0–80%	Tin s.s. + lead s.s.	2.45–2.51	[2]
	80–98%	Tin s.s. + lead s.s.	2.51–2.95	[2]
	98–100%	Lead s.s.	2.95	[2]
Sb	0–40%	Tin s.s. + SbSn	2.45–2.65	[2]
	40–60%	SbSn	2.65–2.67	[2]
	60–94%	SbSn + Antimony s.s.	2.67–2.48	[2]
	94–100	Antimony s.s.	2.48	[2]
	50%	SbSn	2.53	[4]
Bi	0–100%	Tin s.s. + Bismuth s.s.	2.45–2.51	[2]
Pt	25%	Pt_3Sn	1.46	[5]
	50%	PtSn	1.78	[5]
	60%	Pt_2Sn_3	2.09	[5]
	66%	$PtSn_2$	2.05	[5]
	80%	$PtSn_4$	2.45	[5]
	50%	PtSn?	1.51	[4]
As	50%	SnAs	2.40	[4]
Te	50%	SnTe?	3.24	[4]
Mn	20%	Mn_4Sn	1.80	[28]
Mg	33%	Mg_2Sn	1.73	[28]
Nb	25%	Nb_3Sn	1.71	[28]
V	25%	V_3Sn	1.73	[28]
	100%	β-Tin	2.45	[2]

s.s. = solid solution.

the available free space to accomodate these electrons in the metal conduction bands. The ability to do the latter must be influenced by the bonding in compounds. The shifts for the nickel–tin intermetallic compounds studied in this work, for example, increase with percentage tin. This can be explained in terms of less "5s"- electron density per tin atom being donated to the transition metal d-band system as more tin electrons become available with increasing tin content in the binary alloys. Similar results have been obtained from the compounds of the Pd–Sn alloy system [1] (see Table II).

The chemical shift of any series of alloys with the same tin:metal ratio must depend upon the extent to which the tin electrons are used up in band population. The chemical shift will, therefore, be affected by two competing factors:

(1) the lower affinity for electrons from the tin with increasing d electron population of the transition metal within the same row, which will tend to increase the shift;

(2) the lower energy of the d-orbitals with increasing d-electron populations which will lower the energy of the d-bands and increase the use of tin electrons thus decreasing the shift.

Examples of this type of behaviour are clearly seen in Table II and, in the present work for Ni_3Sn and Cu_3Sn, the first effect must be dominant. The lower shifts are connected with the greater amounts of tin electron-density per tin atom required by the less populated d-bands.

An increase in chemical shift for a given alloy composition is also observed with increasing transition metal atomic number in each group. This is consistent with the higher energy expected for the 4d- and 5d- bands. The energies for the 4d- and 5d-bands for the neutral atoms are known to be very similar and it would seem from the Mössbauer data that this is also true for the binary intermetallic compounds.

In the binary tin compounds with the p-block elements, the band that is being filled is presumed to be a valence shell p-band. As the p-block is traversed from the system indium/tin to tin itself, then tin/antimony, tin/tellurium, tin/iodine, the shift gets progressively larger, with the increasing numbers of p-electrons available for the p-bands.

We have, however, shown in earlier papers [6, 7] that tin (II) non-bonding electrons can be donated into non-valence shell bands in approximately close packed structures. Such a process enables the tin (II) ions to be in high symmetry environments without distortion. Compounds showing this effect have novel conduction properties and are identified by very narrow Mössbauer resonance lines that have lower chemical isomer shifts than would be expected for high-symmetry environments.

Loss of electron density from tin into bands in compounds with the p-block elements could, therefore, involve either valence shell p-bands or non-valence shell d-bands. Compounds in which the p-bands are likely to be completely filled (e.g. halides) use the non-valence shell bands while those with a deficiency of p-electrons (e.g. indium/tin) make use of the valence shell p-band. These two mechanisms of band population are reflected in their electrical conduction, e.g. metallic in indium/tin and pseudo-metallic in $CsSnBr_3$.

Tin itself exists in two allotropes, α- tin which is cubic [8] and has a density of 5.76 g cm^{-3}, and β- tin, tetragonal [9] with a density of 7.28 g cm^{-3}. The lower density of α-Sn must reflect a poorer band formation in a material with fewer tin atoms per unit volume to populate that band. The increase in shift in going from α-tin to β-tin must, therefore, result from three factors:

(1) the increased minimum bond length from 2.18 to 3.20 Å which would increase s-electron density;

(2) the increased co-ordination from tetrahedral in α-tin to distorted six co-ordinated, which would also increase s-electron density; and

(3) the greater loss of s-electron density to a band structure with increase of density of the material.

Such a loss is confirmed by studies of the Mössbauer data for β-tin under pressures greater than 1 atm [10]. Further information on the band nature of bulk β-tin is obtained from the work of Bos and Howe [11], on a matrix-isolated tin species in which the chemical shift decreases as the isolated tin atoms grow into polymers, showing s-electron donation to the type ~~of~~ orbital system from which the bands are formed.

The ^{119}Sn Mössbauer data also provide information on the electronic environments of the tin atoms. Electronic environments in tin-containing material do not neccesarily directly reflect the crystallographic environments. To interpret the Mössbauer data only in relation to known structure is restrictive and can cause built-in bias. To attempt to analyse the data to give bonding information at the molecular orbital level is dangerous in the solid state where one is not dealing with isolated molecules and where band structures are relevent. It is, therefore, important in discussing Mössbauer results to consider the total use of the Mössbauer elements' electron density within bonding orbitals and within band populations.

The presence or absence of a quadrupole splitting of the Mössbauer line and its extent, however, gives data on the electronic environment which can be related to the symmetry of the crystallographic site for the atom. A single line in the Mössbauer spectrum means that the tin atom is in a symmetrical electronic environment as in the alloys number 1–3, 8, 9, 11, 12, 15–17, and 20 in Table I. Many of these alloys are known to have symmetrical crystallographic co-ordinations, e.g. [1,3,8,9,11–14,16,17]. The Mössbauer spectra showing quadrupole splitting 4, 5, 13, 14 are those of materials known to have asymmetric crystallographic sites, and here these are reflected in their distortion of the electronic environments.

2.1. The tin environment in the nickel–tin system

In Ni_3Sn the tin occupies a trigonal bipyrimidal site between two equally spaced planar rings of three nickel atoms [12]. This highly symmetrical crystallographic site shows itself in the Mössbauer spectrum as a narrow single line indicating a high electronic symmetry for the site.

Tin, in the intermetallic compound Ni_3Sn_2, also occupies a highly symmetric biprymidal crystallographic site. The composition is, however, very non-stoichiometric with an appreciable deficiency of tin atoms. Every tin atom is surrounded by six nearest neighbour nickel atoms but only four tin atoms surround each nickel creating a highly unsymmetrical crystallographic environment at the nickel atom positions [12]. The tin Mössbauer spectrum for this compound shows quadrupole splitting indicative of a non-symmetrical electronic environment at the tin site. This means that crystallographic imbalance at the nickel atom position must result from its general overall asymmetric electronic distribution which results in the quadrupole splitting of the tin resonance line.

There are two tin environments in the compound Ni_3Sn_4 both of which are distorted [12]. One is a distorted square pyramid of four near-planar nickel atoms opposed by a very short tin–tin bond, the second atom of which is itself associated with four other nickel atoms in the same environment is that of a distorted trigonal pyramid with the tin atom at its centre. A symmetrical doublet is found in the Mössbauer spectrum indicative of a distorted tin electronic environment. From the appearance of the spectrum it would seem that on both sites the electronic environments are distorted to a similar extent.

It is possible to produce by electroplating, hard, bright, corrosion resistant deposits which have found extensive commercial applications. These are usually metastable phases which even when of composition corresponding to equilibrium phases, do not exhibit the same structures as their equilibrium counterparts. X-ray diffraction patterns from these deposits show broad diffuse lines which have not allowed unambiguous characterization of the deposit's structure. It has been the source of some discussion as to whether the compounds of the deposits are distorted by gross compositional differences within the deposit or whether the broad diffractions bands are merely an indication of an extremely fine crystallite size. The nature of tin in these electroplated phases may, however, also be inferred from their Mössbauer parameters. Rooksby's assignment [13] of the diffraction pattern of powdered electroplated nickel tin to a NiAs type structure strongly suggests that it should have a crystallographic environment similar to that of Ni_3Sn_2. The present Mössbauer results show that the electronic environment is very close to that of Ni_3Sn_4 and this, taken in conjunction with the 1 : 1 atomic composition of the electrodeposit, would indicate that the tin atom at least is probably located in a distorted symmetry site and that the line broadening in the X-ray diffraction pattern is due to this cause. It would seem that the method of production of this compound is such that the applied electrical field as the sample is produced is being superimposed on the natural but non-uniform internal field of Ni_3Sn_2, allowing this to incorporate extra tin atoms. These tin atoms cause distortion both crystallographically and electronically resulting in the unusual properties observed.

It is also interesting to note that the effect of plating at different current densities manifests itself as an isomer shift as the examples in Table I show. Since plating at different current densities alters the internal stressing of the coating, this shift must be due to physical displacement of s-electron density due to applied pressure and is hence a direct observation of the magnitude of such stresses. Previously such stresses have been inferred by the deflection produced on a thin copper sheet by a standard thickness of coating.

2.2. The tin environment in the copper–tin system

The compound Cu_3Sn has tin atoms surrounded by six copper atoms in a planar ring and six copper atoms each at the vertices of a trigonal prism with the tin atom at its centre [15]. The Mössbauer spectrum is a very narrow single band consistent with a symmetrical electronic envirenment closely mirroring the crystallographic symmetry. Cu_6Sn_5

is, on the other hand, a compound with the nickel arsenide sturcture [15], which is deficient in tin. Each tin atom is surrounded by six copper atoms but each copper atom is surrounded on average by only five tin atoms. The Mössbauer spectrum consists of a very broad singlet with a higher chemical shift than Cu_3Sn. So, as with Ni_3Sn_2, the electronic environment of the tin site cannot be fully symmetrical as evidenced by the width of the Mössbauer resonance line but without the extreme electronic distortion experienced by nickel, as this compound does not show resolvable splitting.

In the case of the electroplated copper–tin alloy, the X-ray data showed broad diffuse lines which have been indexed as representing a nickel arsenide structure [16]. Examination of the pattern shows, however, that should the diffuse nature of the lines be due to strain or small grain size then the lines observed all correspond to the strongest lines of the Cu_6Sn_5 structure. The composition of the electrodeposit corresponds to that of the compound Cu_3Sn and this is the compound to which it transforms when heated. The Mössbauer data show a very wide single peak with a chemical shift midway between those of the two equilibrium compounds. The line width suggests a strong similarity with Cu_6Sn_5 possibly with even greater electronic symmetry distortion at the tin site, whilst the lower chemical shift is expected, as fewer tin atoms have each to make a greater contribution to the d-band. This seems to confirm that the structure of the as-plated electroplate is very similar to that of Cu_6Sn_5. Also it suggests that the presence of an applied field during the compounds formation has forced a modification of the Cu_6Sn_5 structure on to a composition of Cu_3Sn suggesting, as in the case of the Ni–Sn electroplate, that the presence of an applied field modifies the compound so that an otherwise non-equilibrium phase is produced.

2.3. Silver tin

The tin environment in Ag_3Sn is that of an almost ideal twelve-fold cubic co-ordination but with slight variation between the tin–silver bond lengths [17]. The Mössbauer data show a high chemical shift, larger than for Cu_3Sn, indicating greater s-electron density on the tin in keeping with the superior conductivity of silver requiring less s-electron donation from the tin atoms into the conduction band than is required by copper in Cu_3Sn. The very narrow Mössbauer resonance line for this compound shows a highly symmetrical electronic tin environment.

2.4. Cobalt–tin electroplate

Experimental work on other electroplating systems has shown that it is possible to electroplate a 1 : 1 composition cobalt–tin alloy and that this has a cubic X-ray diffraction powder pattern which was not as diffuse as either the nickel/tin or copper/tin electroplates and whose structure [18] did not resemble those of any equilibrium phases in the system. The Mössbauer data show up a distorted tin electronic environment as that of a quadrupole split spectrum. It would seem most likely that this phase is also a result of modification caused by the application of an applied field during its formation.

2.5. Antimony–tin system

Four samples of antimony-tin compound SbSn with tin percentages 53%, 51%, 48% and 43%, were examined. These compounds all fall within a single intermetallic compound phase field in the binary system and exhibit very slight but progressive rhombohedral distortion from a cubic structure [19]. It was not known whether the substitution of tin by antimony was through specific sites or was by random replacement. The Mössbauer spectrum showed narrow single peaks with very little difference between chemical isomer shifts across the series. This first indicates highly symmetrical electronic environments and the similarity of chemical shift data is indicative of a random substitution of one element by the other.

2.6. Other systems

The tin environment in both SnS [20] and the room temperature form of SnSe [20] are distorted trigonal pyramids. The Mössbauer spectra of these compounds show quadruple splittings which probably reflect their crystallographic environments. The Mössbauer spectra for high temperature SnSe [22] and for SnTe [22] are single resonance lines indicating symmetrical electronic environments, both these compounds are said to have octahedral tin sites in sodium chloride type structures.

It is known that SnTe is a better electric conductor than GeTe or PbTe and that a composition of the type $Pb_xSn_{(1-x)}Te$ $(x < 1)$ is a still better electrical conductor. This has never been satisfactorily explained. From the relatively low chemical shift of SnTe, which is nominally an Sn (II) compound, much of its s-electron density must be in the conduction band. In earlier work we have shown that the electrical conduction of a material depends on the amount of electron density in the band and the distance between atoms for orbital overlap [6, 7, 24]. From the fact that the order of magnitude of conduction of the parents is GeTe < SnTe > PbTe, it appears that the critical distance of overlap is best for the SnTe–PbTe compound. Thus it is dependent on the orbital overlap distance, on the s-electron donation and for the latter "5s" is better donated to 5p or 4d bands than is "4s" or "6s" electron density.

The change in the line width of the Mössbauer spectra observed as one changes temperature from liquid nitrogen temperature to room temperature has been noted by us in the past [25] and we have interpreted this as a more symmetrical Sn electronic environment at the higher temperature.

3. Conclusion

The Mössbauer parameters of the binary tin intermetallics examined can be explained on the basis of an electron band theory as applied to other tin compounds whilst examination of the electroplates yields some indications as to possible reasons for their unusual structures and properties.

Acknowledgement

The authors are indebted to the Tin Research Institute for permission to publish this paper.

References

1. M. CORDEY-HAYES and T. R. HARRIS, *Phys. Letters* **24A** (1967) 80.
2. F. POBELL, *Phys. Stat. Sol.* **13** (1966) 509.
3. R. N. KUZMIN. C. B. NIKITINA and O. KHERCZNER, *Vest. Mosk. Univ. Phys. Astron.* **24** (5) (1969) 11.
4. V. A. BRYUKHANOV, N. N. DELYAGIN. R. N. KUZMIN and V. S. SHPINEL, *Sov. Phys. JETP* **19** (1964) 1344.
5. C. R. KANEKAR, K. R. P. RAO and V. U. S. RAO, *Phys. Letters* **19** (1965) 95.
6. J. D. DONALDSON and J. SILVER, *Inorg. Nucl. Chem. Letters* **10** (1974) 537.
7. J. D. DONALDSON, J. SILVER and (in part) S. HADJIMINOLIS and S. D. ROSS, *J. C. S. Dalton* (1973) 1810.
8. E. R. JETTE and FOOTE, *J. Chem Phys.* **3** (1935) 605.
9. A. IEVINS, M. STRAUMANIS and K. KARLSONS, *Z. Physica* **40B** (1938) 347.
10. H. S. MOLLER and R. Z. MÖSSBAUER, *Phys. Letters* **24A** (1967) 416.
11. A. BOS and A. T. HOWE, *Faraday Trans. II* **70** (1974) 451.
12. O. NIAL, Ph.D thesis, Stockholm, 1945.
13. H. P. ROOKSBY, *J. Electrodep. Tech. Soc.* **27** (1951) 153.
14. A. WESTGREN and G. PHRAGREN, *Z. Anorg. Chem.* **175** (1928) 80.
15. H. KNODLER, *Metall* **20** (8) (1966) 823.
16. H. P. ROOKSBY, *J. Electrodep. Tech. Soc.* **26** (1950) 119.
17. C. W. FAIRHURST and J. B. COHEN, *Acta Cryst.* **B28** (2) (1972) 371.
18. M. CLARKE, R. G. ELBOURNE and C. A. MACKAY, *Trans. Inst. Metal Finishing* **50** (1972) 4.
19. C. A. MACKAY, *J. Appl. Cryst.* **2** (6) (1969) 295.
20. W. HOFMANN, *Z. Krist.* **92** (1935) 161.
21. A. OKAZAKI and I. UEDA, *J. Phys. Soc. Japan* **11** (1956) 470.
22. L. S. PALATNIC and V. V. LEVITAN, *Dokl. Akad. Nauk SSSR* **96** (1954) 975.
23. A. J. PANSER, *Inorg. Chem.* **3** (1964) 940.
24. J. D. DONALDSON, D. LAUGHLIN, S. D. ROSS and J. SILVER, *J. C. S. Dalton* (1973) 1985.
25. J. BARRETT, S. R. A. BIRD, J. D. DONALDSON and J. SILVER, *J. Chem. Soc.* **A** (1971) 3105.
26. V. I. NIKOLAEV, Y. I. SHCHERBINA and S. S. YAKIMOU, *Sov. Phys. JETP* **18** (1964) 878.

Received 9 September and accepted 12 November 1975.