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Stacking disorder in metastable $NiSn_4$

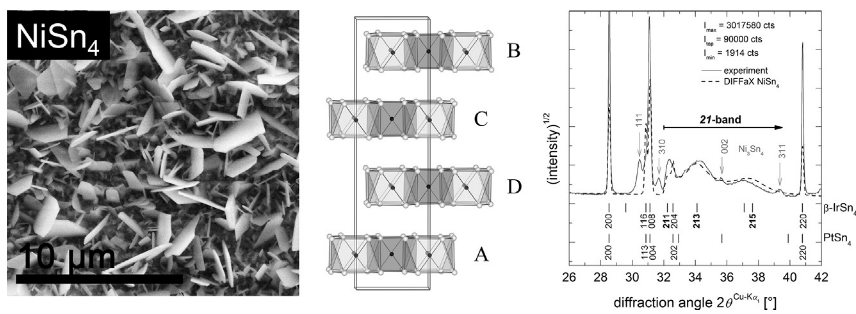
C. Schimpf [a], P. Kalanke [a], S.L. Shang [b], Z.K. Liu [b], A. Leineweber [a,*]

[a] Institute of Materials Science, TU Bergakademie Freiberg, Gustav-Zeuner-Strasse 5, 09599 Freiberg, Germany
[b] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

HIGHLIGHTS

- Growth of metastable $NiSn_4$ in Sn/Ni diffusion couples produced in different ways
- Clarification of the crystal structure of $NiSn_4$
- Modelling of X-ray diffraction patterns of faulted $NiSn_4$ fully explaining the observed patterns
- Critical review of previously published reports on $NiSn_4$

GRAPHICAL ABSTRACT



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ABSTRACT

The atomic structure of $NiSn_4$ intermetallic forming at ambient temperature in different types of Sn/Ni diffusion couples was investigated by powder X-ray diffraction. The recorded diffraction patterns show narrow Bragg reflections as well as characteristic broad diffraction bands indicative of stacking disorder in the crystal structure of $NiSn_4$. The crystal structure consists of *$NiSn_4$ layers* with square-antiprismatic coordination of Ni by Sn. The stacking of these layers is irregular (faulted) by being an intermediate between the pseudotetragonal $PtSn_4$- (space group *Aeaa*) and the tetragonal β-$IrSn_4$-type (space group $I4_1/acd$) ideal structures. Thereby, the shape of the diffraction bands reveals that the stacking more closely corresponds to β-$IrSn_4$- than to the $PtSn_4$-type. The obtained lattice parameters are: $a(\beta\text{-IrSn}_4) = a(\text{PtSn}_4) = b(\text{PtSn}_4) = (6.248 \pm 0.001)$ Å and $2c(\text{PtSn}_4) = c(\beta\text{-IrSn}_4) = (23.001 \pm 0.004)$ Å. Pronounced stacking corresponding to a $PtPb_4$-type structure discussed in the literature is not present in $NiSn_4$ on the basis of the diffraction data. The latter finding is compatible with density functional theory (DFT) based first-principles calculations, indicating a higher energy for $PtPb_4$-type $NiSn_4$ as compared to $PtSn_4$- and β-$IrSn_4$-type $NiSn_4$.

1. Introduction

Upon soldering of copper-containing systems using Sn-based solders, thin Ni buffer layers are frequently used as diffusion barriers in order to avoid excessive formation of Cu_6Sn_5 intermetallic, which can grow rapidly into the Sn, even below the melting point of the solder. This growth is considered as one possible cause for detrimental Sn-whisker formation [1–3]. Nevertheless, also from such Ni buffer layers, Ni–Sn intermetallics can grow into the Sn even at ambient temperature, albeit with a much smaller rate than it is observed for growth of Cu–Sn intermetallics. In solid Sn/Ni couples, formation of Ni_3Sn_4, being the most Sn-rich stable intermetallic in the Ni-Sn system [4,5], is encountered, in particular at elevated temperatures below the melting point of the Sn-rich eutectic. At lower temperatures, down to ambient temperature, at least one additional Sn-rich phase develops.

Most experimental information on Sn-rich intermetallics, apart from Ni_3Sn_4, seems to be compatible with a phase nowadays usually

* Corresponding author.
E-mail address: andreas.leineweber@iww.tu-freiberg.de (A. Leineweber).

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designated as $NiSn_4$ based on its assessed chemical composition.[1] The $NiSn_4$ phase does not only form in solid Sn/Ni diffusion couples [6–9], but was also observed in solidified Sn-rich Ni-Sn melts [10,11] and electrodeposited Sn-rich Ni-Sn alloys [12,13]. $NiSn_4$ has not been included in any Ni-Sn phase diagram as an equilibrium phase, because experimental evidence indicates that the $NiSn_4$ phase is metastable at all temperatures with respect to the tin solid solution and the Ni_3Sn_4 phase [6, 10,12].

The first crystal structure information on the $NiSn_4$ phase was reported by Watanabe et al. [12], who derived a tetragonal unit cell with $a = 6.23$ Å and $c = 5.77$ Å (cf. Table 1) from powder-X-ray diffraction (P-XRD) data recorded from an electrodeposited Ni-Sn alloy. Independently, Boettinger et al. [7] analysed electron backscatter diffraction (EBSD) patterns from $NiSn_4$ grown in a solid Sn/Ni couple and suggested that the crystal structure may be of the $PtSn_4$ type [14]. This structure type is also known for the binary intermetallics $PdSn_4$ [15], (α-)$IrSn_4$ [16], $AuSn_4$ [14], and $CoSn_4$ [17]; for structure details of all structure candidates for $NiSn_4$, cf. Section 2. The structure model for $NiSn_4$ used to interpret the observed Kikuchi lines was derived from those of $PdSn_4$ and $PtSn_4$ with lattice parameters modified due to the substitution of Pd/Pt by Ni; cf. Table 1. Thereby, Boettinger et al. [7] relied on crystal structure data of $PdSn_4$, $PtSn_4$ and $AuSn_4$ from the literature, which had been given in *Aba*2 symmetry, originating from the structure determination of $PtSn_4$ [14]. However, it was suggested [7] that the atomic structure is compatible with a higher, centrosymmetric *Ccca* (*Ccce*) symmetry, which corresponds to a space-group symbol *Aeaa*, if the original choice of basis vectors from Ref. [14] is adopted. Although the inversion symmetry associated with *Aeaa*/*Ccce* was not taken into account in a couple of later works on $NiSn_4$ referring to Boettinger et al. [7], the presence of a higher symmetry for phases of the $PtSn_4$-type had been proposed even earlier: e.g. for $PdSn_4$ [18][2] and for $PtSn_4$ [19]. That higher symmetry was also employed in the structure analysis of the Ni-substitution variants of $AuSn_4$ (maximum Ni content $Au_{0.5}Ni_{0.5}Sn_4$ [20]) and $PdSn_4$ (maximum Ni content $Ni_{0.4}Pd_{0.6}Sn_4$ [19]), which confirm that the orthorhombic $PtSn_4$-type structure may indeed be a very appropriate structure candidate for the metastable $NiSn_4$ phase.

Independently from Watanabe et al. [12] and Boettinger et al. [7], Zhang et al. [9] interpreted P-XRD data from the $NiSn_4$ phase in terms of a tetragonal unit cell with $a = 4.421$ Å and $c = 11.469$ Å (cf. Table 1), where the observed reflections appeared compatible with the *I*4/*mcm* space group symmetry. An atomic structure was, however, not proposed. Moreover, some broad and diffuse diffracted-intensity maxima in the range of $2\theta = 32\ldots40°$ (Cu-Kα radiation) were observed and attributed to some secondary (oxide) phase.

Very recently Liu et al. [21] reported a "metastable phase of Sn". Composition and synchrotron-X-ray microdiffraction data, however, were evaluated in terms of presence of a $NiSn_4$-related phase with $PtSn_4$-type structure with *Aba*2 symmetry yielding the lattice parameters given in Table 1.

Total-energy calculations pertaining to 0 K using density-functional theory (DFT) [22,23] on Ni–Sn phases involved for $NiSn_4$ the $PtSn_4$-type structure in *Aba*2 symmetry[3] and the tetragonal $PtPb_4$ structure [24] (see also Section 2 for structure details). Consideration of the latter was motivated by the tetragonal unit cell reported by Watanabe et al. [12], which is well compatible with the $PtPb_4$ structure type, as well as by the report of a metastable $AuSn_4$ polymorph with $PtPb_4$ structure [25]. These DFT calculations revealed similar energies for $PtSn_4$- and $PtPb_4$-type $NiSn_4$, favouring nevertheless the former. However, the

Table 1
Proposed space groups, crystal structure types and lattice parameters of the crystal structure of $NiSn_4$ found in the literature.

Symmetry	Structure type	*a* [Å]	*b* [Å]	*c* [Å]	Method	Ref.
Tetragonal	None	6.23	6.23	5.77	P-XRD[a]	[12]
Aeaa	$PtSn_4$	6.397	6.426	11.381	EBSD[b]	[7]
*Aba*2	$PtSn_4$	6.171	6.199	11.296	DFT/LDA[c,g]	[22]
*Aba*2	$PtSn_4$	6.347	6.369	11.66	DFT/GGA[d,g]	[22]
*P*4/*nbm*	$PtPb_4$	6.156	6.156	5.726	DFT/LDA[c]	[22]
*P*4/*nbm*	$PtPb_4$	6.325	6.325	5.901	DFT/GGA[d]	[22]
*I*4/*mcm*	None	4.421	4.421	11.469	P-XRD[a]	[9]
Orthorhombic	None	6.25	6.27	–	TEM[e]	[28]
*Aba*2	$PtSn_4$	6.38… 6.40	6.42… 6.43	11.27… 11.49	EBSD[b]	[8]
*Aba*2	$PtSn_4$	6.35	6.39	11.47	S-XRD[f]	[21]

[a] Refinement of powder XRD pattern.
[b] Indexing of Kikuchi patterns with lattice parameters taken from database entries for the 'isomorphous' structure types $PdSn_4$, $PtSn_4$ and $AuSn_4$. The lattice parameter was not refined during Kikuchi pattern indexing.
[c] Calculation using density functional theory (VASP [29]) with local-density approximation.
[d] Calculation using density functional theory (VASP [29]) with generalized-gradient approximation.
[e] Calculated from distance between diffraction spots in TEM selected-area electron diffraction (SAED) patterns.
[f] Synchrotron radiation micro-beam X-ray diffraction.
[g] Similar results were obtained in Ref. [23].

closely related β-$IrSn_4$-type structure [26], which is also known for β-$RhSn_4$ [27], was not considered in the course of the DFT calculations [22].

Although the proposal that the $NiSn_4$ phase exhibits a $PtSn_4$-type structure seems convincing on the basis of EBSD data [7] and the DFT calculations [22,23], there are, nevertheless, observations shedding some doubt on the completeness or even correctness of the structure model for $NiSn_4$. Particularly, Belyakov [28] mentioned that his EBSD patterns lack certain Kikuchi lines, which are predicted to be well visible by the $PtSn_4$ structure model.

As will be shown in the present paper, the above-mentioned inconsistency of the $PtSn_4$-structure model with some experimental evidence can be explained by a modified structure model for the $NiSn_4$ grown in solid Sn/Ni diffusion couples at ambient temperature. That structure model, derived here on the basis of P-XRD data, is a layered one with a layer stacking in-between the previously proposed $PtSn_4$ structure and the closely related tetragonal β-$IrSn_4$-type polytype. Furthermore, DFT calculations are presented, which indicate that the $PtSn_4$-type and β-$IrSn_4$-type structures have virtually identical energies, which are significantly lower than that for the $PtPb_4$ structure. In fact, the latter structure appears incompatible with the P-XRD results.

2. Structure systematics of $NiSn_4$-related layered *T*Sn_4 phases (*T*: transition metal)

The $PtPb_4$-, $PtSn_4$-, and β-$IrSn_4$-type structures regarded as relevant for the $NiSn_4$ intermetallic in the present work are illustrated in Fig. 1. In all these potential $NiSn_4$ structures Ni is coordinated by a square-antiprism formed by 8 Sn atoms [26]. These $NiSn_8$ square-antiprisms share common edges forming layers resulting in the $NiSn_4$ composition of the layers and in arbitrary stacking variants of these layers. These layers will be referred to as *$NiSn_4$ layers* henceforth, an example of which seen from [001] is shown in Fig. 1a. In all structures the stacking direction is [001], which is ensured in the case of the orthorhombic $PtSn_4$-type structure by an appropriate choice of the basis vectors in the non-standard *Aeaa* setting of space group no. 68. Note that the *Ccce*/*Ccca* standard setting has been used in a couple of previous works [7,15,20].

[1] Note that in some of the early works this phase was also denoted with the formula $NiSn_3$, e.g. [6].
[2] In the same work it was supposed that for $AuSn_4$ the *Aba*2 symmetry might indeed be correct.
[3] Inspection of the relaxed atomic coordinates from Refs. [22,23] reveals that these are compatible with the centrosymmetric *Aeaa* symmetry.