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$NiSn_4$ formation during the solidification of Sn–Ni alloys

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A B S T R A C T

The growth of $NiSn_4$ is studied during the solidification of Sn–Ni alloys containing 0–0.45wt%Ni. Where past research has found metastable $NiSn_4$ after solid state ageing of Ni–Sn couples, it is shown here that $NiSn_4$ also forms during solidification as both a primary and a eutectic phase over a wide range of solidification conditions. The $NiSn_4$ phase has crystal structure isomorphous to $PtSn_4$ (o*C*20) and no evidence is found for $NiSn_4$ being stable at solidification temperatures. Primary $NiSn_4$ crystal growth was promoted by high cooling rates and a comparison of growth ledges on the facets of primary $NiSn_4$ and Ni_3Sn_4 crystals suggests easier interface attachment kinetics for $NiSn_4$. The Sn–$NiSn_4$ eutectic grew under all solidification conditions used, with an orientation relationship that produces a low lattice disregistry at the interface plane and the same $NiSn_4$ growth direction as that selected during free growth of primary $NiSn_4$. In hyper-eutectic compositions, both the Sn–$NiSn_4$ and Sn–Ni_3Sn_4 eutectics grew with the latter growing from primary Ni_3Sn_4 crystals.

1. Introduction

The Ni–Sn system is important in Pb-free soldering because Ni is a common substrate in electronic packaging and most commercial solders are multicomponent alloys containing at least 95wt% Sn. Ni is often chosen as a substrate in soldering to take advantage of the significantly slower growth kinetics between Ni and Sn than between Cu and Sn. A common approach is to use a Ni layer as a diffusion barrier to prevent molten solders from reacting with Cu substrates or to prolong the shelf life of PCBs with solderable tin plated surface finish.

The equilibrium intermetallics in the Ni–Sn system have been shown to be Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4, with the first two having allotropic modifications [1]. However, Ni–Sn soldered joints and diffusion couples are occasionally reported to contain additional non-equilibrium intermetallics in the reaction zone. For example, 'Ni_3Sn_7' [2], 'Ni_3Sn_8' [3], '$NiSn_3$' [4–8], '$NiSn_4$' [9–11] and '$NiSn_9$' [12] have been reported in (i) solid state heat treated or thermally-cycled Sn/Ni plated layers [3,5,10,11,13], (ii) Sn/Ni reaction couples [4,6,8,9], (iii) solder joints in the as-soldered state [7] and (iv) deposited Sn–Ni alloy coatings [12]. Fig. 1 summarizes past work on the measured compositions of the phases and the stoichiometry proposed by each set of authors. Importantly, most of the proposed stoichiometries are based on composition measurements without crystallographic investigations. Use of quotation marks in this paper indicates such ambiguities and no quotation marks are used when the composition and the crystallography were measured by the individual researcher. Due to these uncertainties, it is not clear whether Fig. 1 contains five different phases.

Two studies that did examine the crystallography are by Boettinger et al. [11] and Watanabe et al. [14]. Boettinger at al. used Electron Backscattered Diffraction (EBSD) to show that the phase with composition Sn-20at%Ni ($NiSn_4$) has prototype o*C*20-$PtSn_4$ and proposed the lattice parameters. Watanabe et al. deduced that a phase with composition Sn ~ 15at%Ni is tetragonal and determined lattice parameters via XRD. Ghosh [15] suspected that this tetragonal phase is t*P*10-$AuSn_4$ and used density functional theory to compare $NiSn_4$ with Pearson symbol o*C*20 and t*P*10. He showed that the thermodynamic stability of the two phases is very similar at 0 K and calculated o*C*20-$NiSn_4$ to be slightly more stable.

In almost all cases, non-equilibrium Ni–Sn intermetallics have been found after solid state ageing of Ni–Sn couples (e.g. soldered joints, plated layers or diffusion couples) and often after thermal cycling at temperatures of $-40\ldots+195$ °C [3–6,8–11,13]. The fastest growth rate of '$NiSn_3$/$NiSn_4$' in reaction couples is reported to be in the range 100–170 °C [3–5,8], and passing an electric current through a solder joint between Ni and Sn has been shown to promote '$NiSn_3$/$NiSn_4$' growth at 100 °C, but not at temperatures above 180 °C [6,9]. Furthermore, the nucleation and growth of the non-equilibrium phases has been found to depend on the nature of the Ni substrate (bright, matte etc.), contaminants and surface

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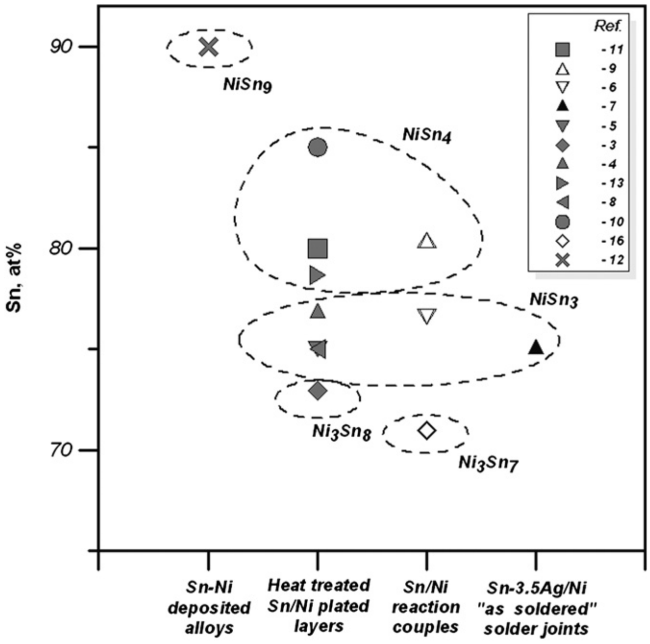

Fig. 1. Measured compositions of reported non-equilibrium Ni-Sn phases. Dashed lines group studies by the stoichiometry proposed by each set of authors.

Table 1
Compositions of the prepared alloys in wt%, as determined by ICP-AES. Detected levels of Cd, Al, Zn, Bi and Ag were <0.001 wt%.

Sample composition	Ni,%	Pb,%	Sb,%	Cu,%	As,%	Fe,%
Commercial purity alloys						
Sn-0.03Ni	0.030	0.025	0.006	0.004	0.002	0.010
Sn-0.08Ni	0.077	0.029	0.009	0.004	0.004	0.011
Sn-0.13Ni	0.129	0.038	0.004	0.005	0.001	0.015
Sn-0.16Ni	0.160	0.032	0.008	0.004	0.001	0.013
Sn-0.2Ni	0.205	0.015	0.005	0.003	0.001	0.004
Sn-0.37Ni	0.375	0.021	0.005	0.003	0.001	0.007
Sn-0.39Ni	0.390	0.018	0.004	0.003	0.001	0.006
Sn-0.45Ni	0.452	0.021	0.005	0.002	0.001	0.008
High purity alloys						
Sn-0.16Ni	0.148	0.0003	0.0003	ND	ND	ND
Sn-0.3Ni	0.300	0.0004	ND	ND	ND	ND

Where ND refers to 'under the detection limit' (<0.0002).

roughness [3,5]. The addition of Co and Pd to the Ni substrate are reported to promote and stabilize the formation of '(Ni,X)Sn_4' (X = Co, Pd), even at temperatures where the solder is liquid [13,16]; whereas Pb additions to the solder inhibit the development of '$NiSn_3$' or completely eliminate it [5]. The only report found of any of the phases in Fig. 1 being formed in the as-soldered condition is Choi et al. [7], who examined '$NiSn_3$' after soldering Ni electroplated Cu substrates with Sn-3.5Ag solder. In their study, the thickness of the Ni coating played an important role in the type of IMC formed at the interface. '$NiSn_3$' formed at 250 °C when the Ni substrate was 2 μm, the thinnest Ni coating used [7].

There are no reported observations to date of these non-equilibrium intermetallic compounds forming in as-cast or equilibrated Sn–Ni alloys. This paper investigates whether any of the phases in Fig. 1 can form during solidification of Sn-rich Sn–Ni alloys, and explores the causes and mechanisms of their formation during the solidification of Sn-rich Sn–Ni alloys.

2. Experimental procedures

Sn–Ni alloys containing 0–0.45 wt%Ni were studied. Most of the research was conducted with commercial purity (CP) alloys, prepared by mixing a commercial Sn-10wt%Ni master alloy with 800 g of 99.9%Sn in a clay-graphite crucible coated with FOSECO dycote, and heating in a resistance furnace to 400 °C. After 1-h at hold, the mixture was stirred with a boron nitride (BN) coated stainless-steel spoon to ensure master alloy dissolution. Additionally, high-purity (HP) alloys were prepared from 99.999%Sn and 99.99%Ni, using high-purity graphite for the crucible and stirring-rod. In this case, a high-purity Sn-10wt%Ni master alloy was first produced by encapsulating Sn and Ni in an evacuated quartz ampoule, and holding at 1200 °C for one week. Samples of both the CP and HP melts were measured by Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Table 1 provides details of the composition of the alloys.

For microstructural characterisation, 70 ± 10 g samples were collected from the melt in BN-coated stainless-steel cups (graphite cups for high-purity samples), similar to the procedure of Ventura et al. [17]. The cups were immersed in the melt at 400 °C for 20 s to ensure the cup and alloy were at the same temperature. Samples were then placed on an insulating board, covered by another insulating board and a BN-coated 1.5 mm K-type thermocouple was placed in the centre of the sample (within a quartz tube for high-purity samples) to monitor the cooling curve as the sample cooled radially in air. This procedure resulted in a cooling rate in the liquid just prior to the nucleation of Sn of about 0.5 K/s (0.25 K/s for high-purity samples).

An additional technique was developed to study the influence of cooling rate on microstructure. Two quartz tubes with inner diameter of 5 mm and wall thickness of 1 mm were fixed at the fan level in the centre of a forced air convection furnace. Samples were produced by drawing 400 °C liquid into quartz tubes of 4 mm inner diameter under vacuum. A sample mass of 0.5 ± 0.05 g was then added to each tube. The first sample had a BN-coated 0.5 mm K-type thermocouple inserted at the centre and the second tube contained a specimen for microstructural analysis. Samples were equilibrated at 390 °C for 1 h before cooling by one of four methods which produced cooling rates (in the liquid prior to the nucleation of Sn) spanning four orders of magnitude. (i) Cooling in an ice-water slurry resulted in rates of 115–120 K/s, (ii) the furnace door fully-open resulted in rates of 1.7–2.6 K/s, (iii) the furnace door partially-open resulted in rates of 0.2–0.5 K/s, and (iv) the furnace door closed resulted in rates of 0.008–0.022 K/s.

To investigate the growth mechanisms of the eutectic, CP Sn-0.13Ni was grown under controlled unidirectional conditions. Samples were produced by drawing 400 °C liquid into quartz tubes of 2.8 mm inner diameter under vacuum. A Bridgman furnace with an induction heated hot zone and Woods metal cold zone was used. A 110 mm sample rod was mounted on a cold finger inside the furnace. The specimen was grown in an argon atmosphere at a pull rate V = 48 μm/s and a temperature gradient at the solid/liquid interface of $G = 7.5$ K/mm. After quenching, the specimens were sectioned at 5 mm and 30 mm from the bottom and both transverse and longitudinal sections were analysed.

To test whether the as-cast phases are equilibrium or metastable phases at solidification temperatures, a portion of the samples were heat treated at temperatures in the range 220–330 °C. Solid state heat treatment was carried out in a resistance furnace. As-cast samples were packed in sand and heat treated for a maximum of 1 month. Heat treatments above the eutectic temperature were carried out in a forced air convection furnace in borosilicate glass test tubes held vertically. The estimated temperature stability in the furnace was of ±0.25 K. After the heat treatment, samples were carefully extracted from the furnace and quenched in water at room temperature.