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# Formation and growth of $Ni_3Sn_4$ intermediate phase in the Ni - Sn system

D. GUR, M. BAMBERGER
*Department of Materials Engineering, TECHNION-Israel, Institute of Technology, Technion, Haifa 32000, Israel*
*E-mail: mtrbam@tx.technion.ac.il*

Dipping experiments of Ni foils in molten tin were made in the temperature range, 280–310°C. In addition, experiments were conducted while passing a constant current through the system, the foils being used as electrodes. In SEM - EDS observations and analysis the $Ni_3Sn_4$ equilibrium intermediate phase was found to grow both as a layer at the solid/liquid interface and as platelets in the melt. Growth kinetics were found to be influenced by the dissolution of Ni in the melt. The voltage between the electrodes vs. time ($V(t)$ curve), measured *in-situ*, was found to conform to SEM observations. The $V(t)$ curves permit a qualitative evaluation of the layer growth process. © *2000 Kluwer Academic Publishers*

## 1. Introduction

Three equilibrium intermediate phases, - $Ni_3Sn$, $Ni_3Sn_2$, and $Ni_3Sn_4$ - exist in the Ni-Sn system [1]. In recent work it was found that $Ni_3Sn_4$ is the only intermediate phase that grows in a diffusion system containing Ni(solid)-Sn(liquid) at temperatures between 235 and 600°C [2]. Fast kinetics were observed, and the diffusion of Ni in liquid Sn was found to control the phase growth. In addition, lateral grain growth in the $Ni_3Sn_4$ layer was seen to accelerate apparently due to the presence of the liquid phase [3].

In this work, Ni foils were dipped in molten tin and the $Ni_3Sn_4$ growth kinetics, were qualitatively evaluated *in situ* on the basis of electrical measurements.

## 2. Experimental procedure

150-micron-thick Ni strips, of dimensions $10 \times 40$ mm$^2$, were cut from 99.5% pure foil. The strips were cleaned in solvents to remove fats, and then heat-treated in an $H_2$ atmosphere in order to reduce the surface oxide layer. Finally, the strips were tin-cladded by warpping them with 99.5% pure Sn foil and then pressed until plastic deformation of the tin occurred and a tight bond was obtained between the Ni and the Sn envelope. This procedure was essential for achieving good wetting and the formation of the reaction layer over the entire dipped surface of the Ni foil. The Sn-cladded Ni strips were mounted in an apparatus by means of which they were immersed in molten Sn (99.9% pure) held in a Pyrex container inside a hot furnance. Test temperatures were in the range, 280–310°C. Copper wires, soldered to the Ni strips, were connected to a voltmeter outside the furnance. The experimental apparatus is shown schematically in Fig. 1.

The system contained two Ni strips, which were also used as electrodes in passing an electrical current through the system. The voltage between the Ni electrodes was measured with a DVM, and voltage vs. time curves - $V(t)$ were obtained.

It was assumed that the electrical resistivity of the $Ni_3Sn_4$ intermediate phase that grows at the solid/liquid interface is higher than that of pure Ni, the Sn melt, and the Cu wires, which are good conductors. Thus, if there is good wetting and growth takes place over the entire immersed surface, then by applying a constant current, the increase in layer thickness will increase the resistance of the system, as show by an increase in the voltage measured between the electrodes. In this way an *in-situ* qualitative evaluation of growth kinetics can be obtained.

Specimens for metallographic examination were prepared from the dipped strips. The preparation proce-

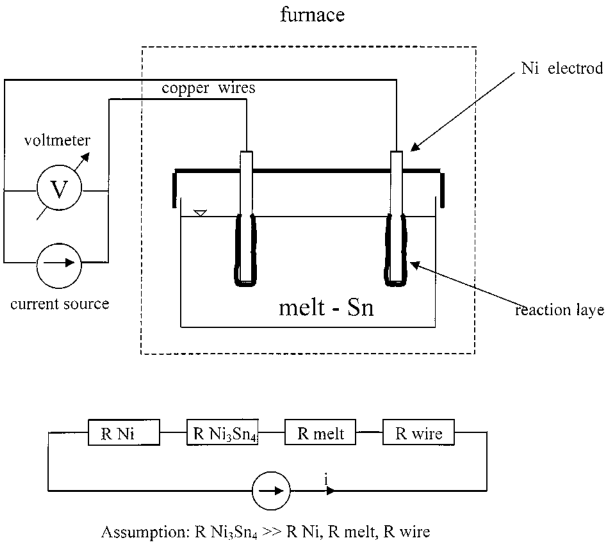

*Figure 1* Apparatus for dipping experiments including *in-situ* electrical measurements.

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dure is described elsewhere [2]. The specimens were analyzed mainly by JEOL JSM-840 scanning electron microscope including a LINK - AN10000 EDS system.

## 3. Results

### 3.1. Experiments performed without applying an electric current

Fig. 2 is a SEM micrograph of a strip dipped for 60 minutes in molten Sn at 300°C. Severe dissolution of the Ni is observed. A very thin layer of the $Ni_3Sn_4$ phase was detected at the Ni/Sn interface and some elongated precipitates of this intermediate phase were present in the melt zone.

By re-using the same melt for several experiments the Ni concentration increases and the dissolution of the strip is less severe. In addition, more plate-like $Ni_3Sn_4$ precipitates were detected in the melt zone, as shown in Fig. 3.

The $Ni_3Sn_4$ layer that grows on the Ni surface is thicker than that produced by pure Sn melt and a tendency to crumble into the melt can be observed.

Fig. 4 presents, at higher magnification than Fig. 3, the crumbling of the $Ni_3Sn_4$ layer grains and the $Ni_3Sn_4$ platelets in the melt zone.

### 3.2. Experiments performed with constant current

Fig. 5 shows a specimen after dipping for 50 minutes in Sn(Ni) at 280°C and the simultaneous application of an electric current through the system. A $Ni_3Sn_4$ layer can be observed near a zone of dissolution pit on the

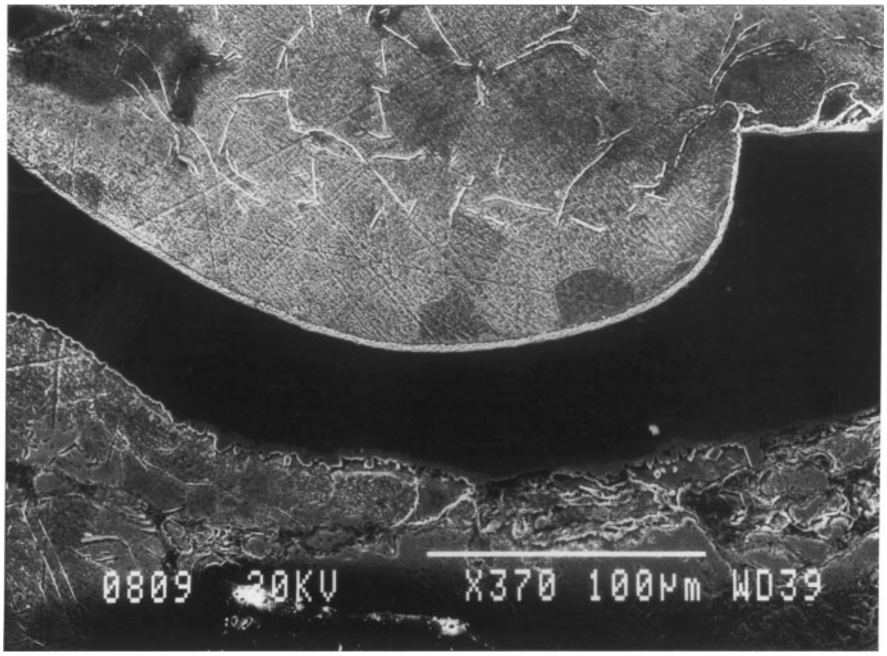


*Figure 2* SEM micrograph of the cross-section of specimen following dipping for 60 minutes in pure molten Sn at 300°C.

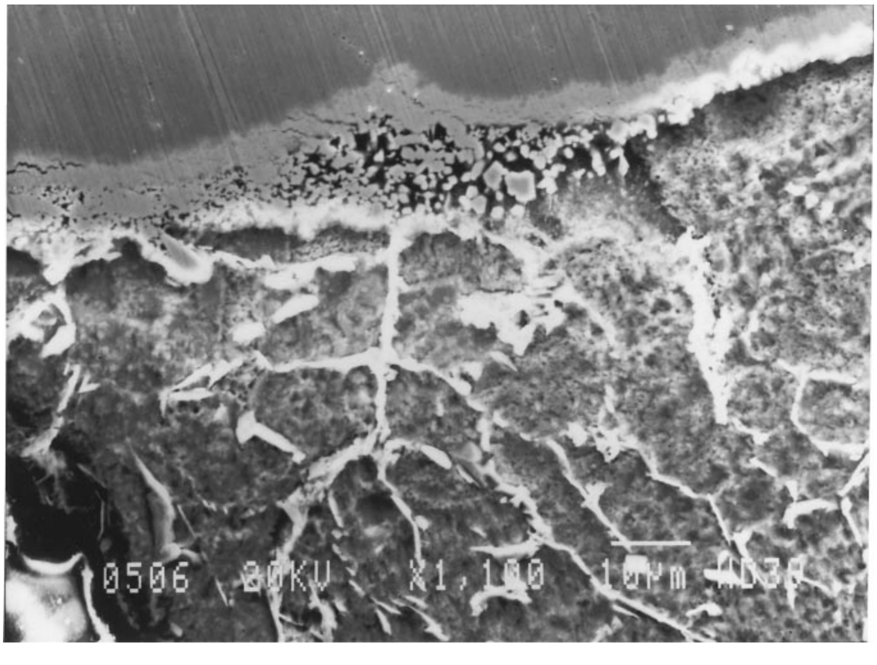
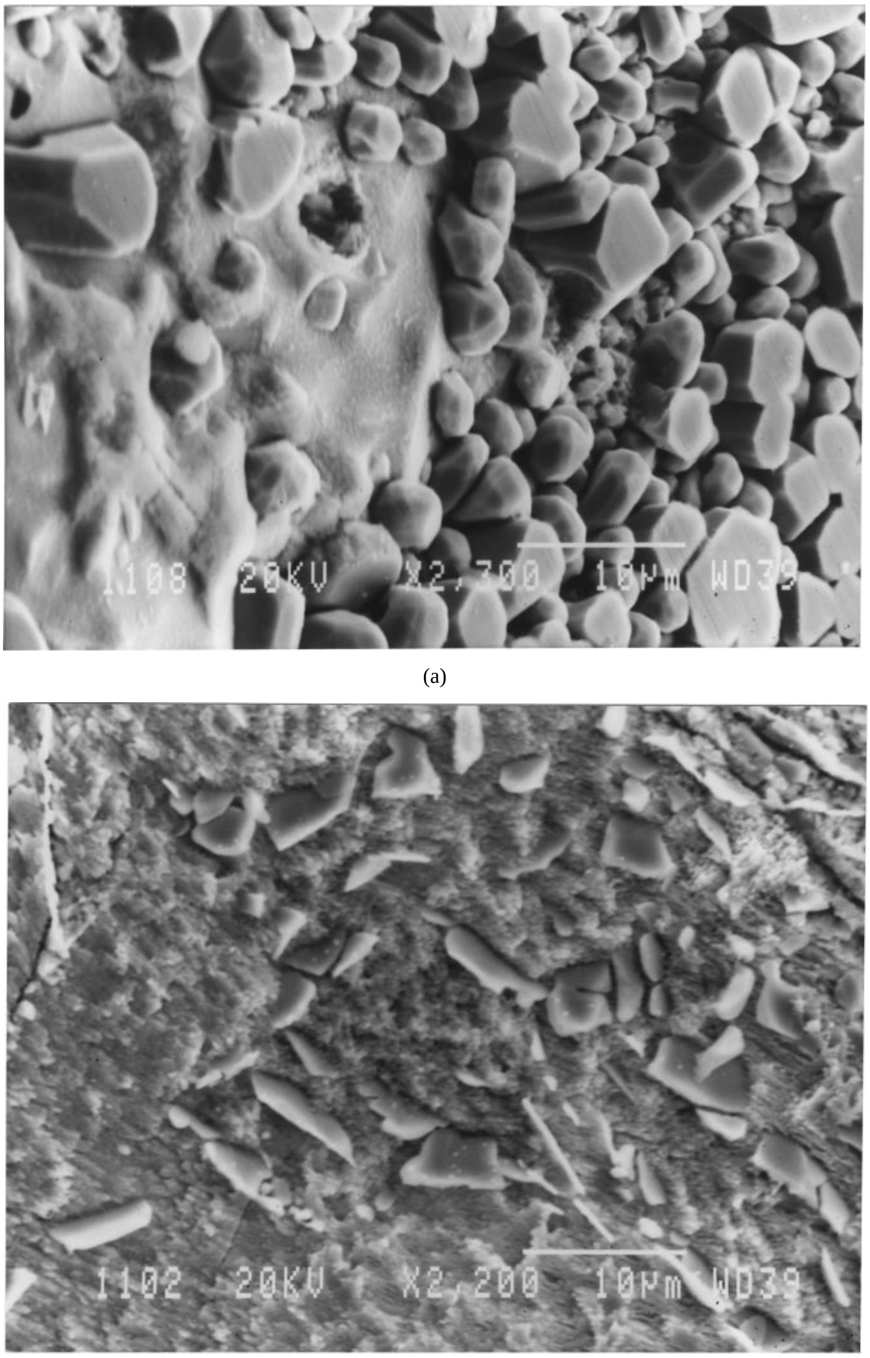


*Figure 3* SEM micrograph of the cross-section of specimen following dipping for 30 minutes in an Sn(Ni) melt at 300°C.



(a)

(b)

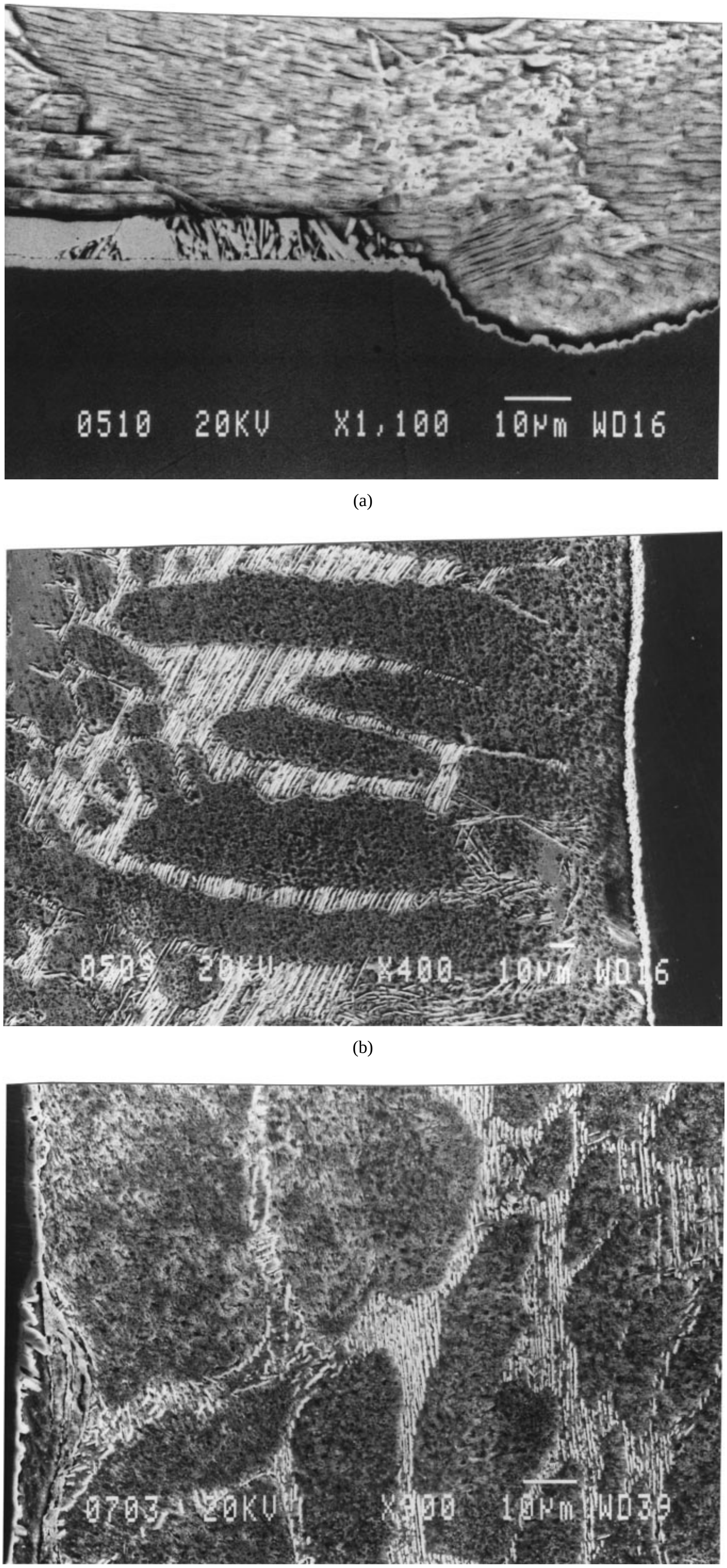
*Figure 4* SEM micrograph of the cross-section of a specimen subjected to the same test conditions as the specimen of Fig. 3, showing (a) the crumbling of $Ni_3Sn_4$ grains into the melt and (b) the plate-like $Ni_3Sn_4$ precipitates in the melt zone.

Ni electrode (Fig. 5a) and the parallel alignment of the $Ni_3Sn_4$ platelets in the melt (Fig. 5b).

Composition measurements through the $Ni_3Sn_4$ layer showed a constant concentration of 57.6 at.% Sn, which corresponds to the concentration of the intermediate phase at equilibrium with liquid Sn(Ni). The composition of the melt in the platelets zone was $96 \pm 1$ at.%Sn, whereas in the platelets-free zones a value of $99.5 \pm 0.5$ at.%Sn was obtained. Fig. 5c depicts the results of the experiment of dipping for 15 minutes in molten Sn(Ni) at 310°C. The parallel alignment of the $Ni_3Sn_4$ platelets in the melt can again be observed.

The $V(t)$ curves obtained from these experiments are presented in Fig. 6. Curve (a) was obtained in an experiment involving a pure Sn melt. In this case strong dissolution of the Ni occurs and a very thin $Ni_3Sn_4$ layer was observed on the electrode surface. The curve shows a fast increase in voltage during the first 6 minutes and then a plateau of constant voltage (similar to saturation).

Curve (b) was obtained from dipping in molten Sn(Ni). In this curve saturation occurs later, viz. after about 15–20 minutes. Curve (c) was obtained from dipping in Sn(Ni), from which the specimen shown in Fig. 5a was obtained. In comparison with other specimens from similar tests the $Ni_3Sn_4$ layer in this case is relatively thick and, in addition, dissolution pits were found on the surface. The corresponding $V(t)$ curve shows no saturation but a monotonic increase of the voltage.

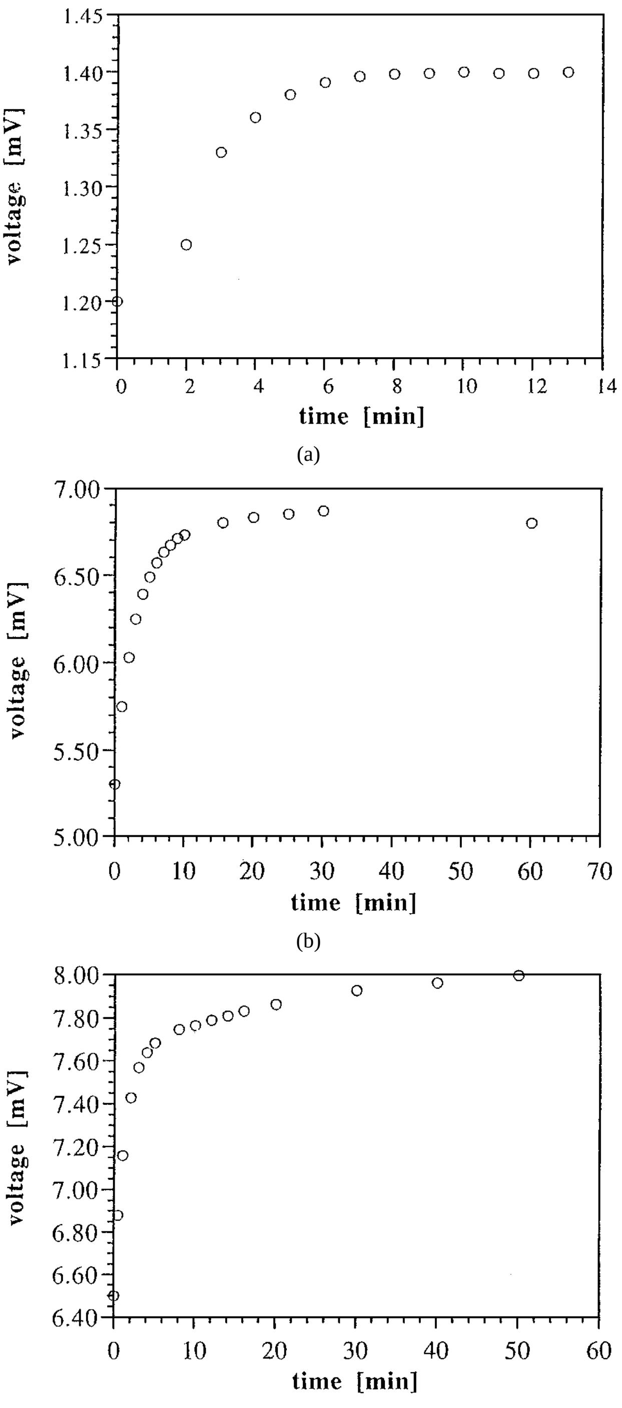


(a)

(b)

(c)

*Figure 5* SEM micrograph of a specimen after dipping in Sn(Ni) melt and simultaneous application of 100 mA electric current during the process (a), (b) at 280°C for 50 minutes and (c) at 310°C for 15 minutes.



(a)

(b)

(c)

*Figure 6* $V(t)$ curves of the dipping experiments in (a) pure Sn melt $I = 20$ mA $T = 290°\text{C}$, (b) Sn(Ni) melt, $I = 100$ mA $T = 300°\text{C}$, (c) Sn(Ni) melt $I = 100$ mA $T = 280°\text{C}$. In all of which the Ni electrode showed a relatively stable $Ni_3Sn_4$ layer and dissolution pits.

## 4. Discussion

The SEM observations of the dissolution and $Ni_3Sn_4$ phase growth on the Ni electrode surface are in agreement with theory [4–11]. The diameter of the melt container was 50 mm. Assuming a diffusuvity in liquid metals of $10^{-9}$ $m^2/s$, yields a diffusion distance of about 2 mm in 60 minutes of experiment. Therefore the diffusion medium can be regarded as infinite. In the experiments with pure Sn melt severe dissolution occurs due to the complete absence of Ni in the melt and the dissolution rate, which is proportional to $\Delta C = Cs - C(t)$ is at a maximum (Cs- melt concentration at saturation, $C(t)$ - concentration at time $t$).

The $V(t)$ curve (Fig. 6a) conforms to the SEM micrographs, which show a fast increase in voltage, which can in turn be related to the fast growth of the $Ni_3Sn_4$ phase in parallel with its dissolution and the achievement of a steady state condition indicated by the saturation voltage. The growth rate of an intermediate-phase layer by diffusion of the Ni through it is inversely proportional to its thickness [11, 12]. This means that if the liquid can be regarded as an infinite medium i.e. that no saturation can be reached, a $Ni_3Sn_4$ layer will grow in parallel with the dissolution until a constant thickness is achieved, in which the rate of growth is equal to the rate of dissolution, namely steady state condition. Experiments performed in an Sn(Ni) melt show less of the dissolution effect and a thicker $Ni_3Sn_4$ layer at the solid/liquid interface. The $V(t)$ curve in this case (Fig. 6b) shows that the saturation voltage was reached after a longer time than with the pure Sn melt. As the initial Ni concentration in the melt - $C(t = 0)$ rises, the dissolution rates during the experiment is smaller, permitting a thicker $Ni_3Sn_4$ layer to form at the interface.

When the Ni concentration in the melt reaches a high level and less dissolution takes place, the thickness of the $Ni_3Sn_4$ layer increases. EDS analysis in its cross-section reveals a uniform composition in the layer, corresponding the concentration in the $Ni_3Sn_4$/Sn(Ni) interface at equilibrium.

The growth of the $Ni_3Sn_4$ layer is controlled by the diffusion of Ni through the melt. This Ni is supplied from the layer grain boundry grooves, at which local dissolution takes place [2]. This local dissolution resulted in the crumbling process, which in turn results in the penetration of the melt into the $Ni_3Sn_4$ grain boundaries and "sweep" the grains (Figs 3 and 4a). Resulting from this process, an apparent reduction of the layer thickness or an apparent steady state can be obtained from the measured layer thickness and it might affect the electrical measurements. As the $Ni_3Sn_4$ grains are detached from the layer and swept into the melt, where they are surrounded by the low-resistivity Sn(Ni), their contribution to the overall resistance is negligible. The apparent steady state, as indicated by the saturation voltage, is therefore obtained due to the crumbling effect, which in turn is due to the local dissolution of the grain boundary grooves and not because of the overall fast dissolution as in the case of experiments with pure Sn melt.

In Fig. 6c the saturation voltage was not attained, and in the SEM observation a more stable $Ni_3Sn_4$ layer was detected (Fig. 5a). The melt in this experiment contained Ni, so that less severe dissolution than in pure Sn melt was expected. In this specimen the crumbling process was less pronounced, a relatively thick layer was obtained, and pitting was observed on the surface. The two effects, of less crumbling and the presence of pitting, may be correlated. If in the vicinity of the dissolution pit a supersaturated melt exists, then the crumbling is less severe. If there is no dissolution, then the Ni required for the growth of the layer is supplied by the grain boundaries of the $Ni_3Sn_4$ [2].

Thus an alternative Ni source could be the dissolution pits. Consequently a reduction in the penetration of the grain boundary grooves and thereby a reduction in the crumbling effect can be obtained. The monotonic increase in electrode voltage is in agreement with such as situation.

The $Ni_3Sn_4$ phase was detected not only as a layer at the solid/liquid interface but also in the melt (Figs 4 and 5). The phase morphology in the melt is plate-like, which is different from the layer grain morphology. Two important observations are made in connection with these platelets:

1. It seems that the platelets were growing in the melt during the experiment, a situation which requires the supersaturation of the melt.
2. There is a well defined alignment of the platelets parallel to each other in some zones of the melt but only when an electrical current is applied to the system.

The presence of supersaturation of the melt far from the Ni electrode can be explained by using the Gibbs-Thomson equation [13]. The actual surface of the $Ni_3Sn_4$ layer is not flat, but rather a curved surface due to the separate grains and the presence of grain boundary grooves. Thus according to the Gibbs-Thomson equation the equilibrium concentration (the chemical potential) of the melt near the interface is higher than that of a flat interface. Then, due to the concentration gradients in the melt, supersaturation may exist in it at places far from the interface. This could be the driving force for the growth of an equilibrium flat-interfaced precipitate - the $Ni_3Sn_4$ platelets.

In order to estimate the degree of supersaturation, the following assumption are made : the solid/liquid interface energy for Sn is 100 erg/cm$^2$, the radius of curvature of a fine spherical grain in the layer is 0.5 micron, and the molar volume is estimated to be 17 cm$^3$/mole. This enables to approximate the difference in chemical potential as 6.7 J/mole, producing a concentration difference of 0.15% relative to a flat interface (assuming $\mu = RT\ \ln X$, in which $\mu$ -chemical potential, $X$-mole fraction, $R, T$- respectively the gas constant and temperature).

This is relatively a low value for supersaturation and may not be enough for nucleation of the platelets, but, it may be sufficient for a slow growth process of small grains which had crumbled from the layer. The reason for the parallel alignment of the platelets is not clear at present. It may be that this alignment enables a more convenient passage of the electrical current. The movement of the platelets is possible because no shear stresses can act on the melt-surrounded platelets. Additional research is needed on this subject.

## 5. Conclusions

Dipping Ni strips in a pure Sn melt results in severe dissolution of the Ni and minor layer growth, whereas in an Sn(Ni) melt the dissolution was less pronounced, enabling the growth of a thicker $Ni_3Sn_4$ layer at the solid/liquid interface. This is in agreement with theories concerning dissolution and diffusion.

The results of electrical measurements confirm the SEM observations and qualitatively indicate the conditions in which: 1) severe dissolution takes place, 2) steady state (saturation) exists and the $Ni_3Sn_4$ layer does not grow, 3) layer thickness in the system increases monotonically. The growth of $Ni_3Sn_4$ platelets in the melt can be explained on the basis of the Gibbs-Thomson equation. It may occur due to supersaturation of the melt far from the solid liquid interface.

Parallel alignment of the platelets was observed in experiments in which an electric current was applied.

## References

1. “Binary Alloy Phase Diagrams Vol. 3” (ASM International, 1992).
2. D. GUR and M. BAMBERGER, *Acta Mater.* **46**(14) (1998) 4917.
3. *Idem.*, Lateral grain growth during reactive isothermal solidification in the Ni-Sn system, to be published.
4. E. A. MOELWYN-HUGHES, “The Kinetics of Reaction in Solution” (Clarendon Press, Oxford, 1947).
5. J. M. LOMMEL and B. CHALMERS, *Trans. of the Metall. Soc. of AIME* **215** (1959) 499.
6. H. NAKAGAWA, C. H. LEE and T. H. NORTH, *Metall. Trans. A* **22A** (1991) 543.
7. I. TUAH-POKU, M. DOLLAR and T. B. MASSALSKI, *ibid.* **19A** (1988) 675.
8. V. N. YEREMENKO *et al.*, *J. Mater. Sci.* **16** (1981) 1748.
9. V. I. DYBKOV, *ibid.* **21** (1986) 3078.
10. *Idem.*, *ibid.* (1990) 3615.
11. G. V. KIDSON, *J. Nuclear Mater.* **3**(1) (1961) 21.
12. J. PHILIBERT, *Defect and Diffusion Forum* **66–69** (1989) 995.
13. P. HASSEN, “Pysical Metallurgy,” 2nd. ed. (Cambridge University Press, 1986).

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