

PHASE TRANSFORMATIONS AT HEATING OF Sn–Ni–Zn POWDERS OBTAINED BY CEMENTATION FROM SOLUTIONS

ФАЗОВЫЕ ПРЕВРАЩЕНИЯ ПРИ ПРОГРЕВЕ ПОРОШКОВ Sn–Ni–Zn, ПОЛУЧЕННЫХ ЦЕМЕНТАЦИЕЙ ИЗ РАСТВОРОВ

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Abstract. The low-temperature method of Sn–Ni–Zn powders synthesis by cementation of tin and nickel with zinc powder from acidic solutions with the formation of “zinc core – porous nickel shell – external tin layer” structures has been proposed. The method provides metals ratio control in wide ranges (7–41 at. % of tin, 38–86 at. % of nickel and 7–24 at. % of zinc) by variation of the process duration. X-ray phase analysis data give evidence on the presence of β -Sn and Zn phases as well as NiZn₃ and NiSn intermetallics in the powders obtained. Differential scanning calorimetry data show the availability of Sn–Zn eutectic with the melting point at 171.2 °C in the powders with high tin content (30–40 at. %). The formation of the ternary intermetallic τ_1 phase (Ni_{3+x}Sn₄Zn) has been established to occur as a result of the powders heating at 260 °C. The discovered low-temperature phase transformation in Sn–Ni–Zn system at 260 °C is of interest for electronic equipment assembly processes that include consecutive stages of soldering and resoldering.

Keywords: CEMENTATION, POWDER, NICKEL, TIN, ZINC, PHASE COMPOSITION, INTERMETALLIC, SOLDER.

1. Introduction

The formation of soldered joint (seam) between the metal to be brazed and the solder heated to a temperature slightly above the solder melting point (T_m) is one of the key stages of the soldering technological process. The formation of intermetallic compounds, solid solutions or eutectics occurs in the seam as a result of the interdiffusion and subsequent crystallization processes. The main requirements for soldered joints are their high mechanical strength and acceptable structural characteristics that provide reliable contact with the surface, corrosion resistance, good thermal and electrical properties as well as the possibility of heat treatment of elements containing such joints without causing damage to them [1]. To fulfill these requirements it is necessary to use solders with definite chemical composition. Powder solders have recently become popular on the world market. Their application provides the reduction of labor intensity in the soldering technological process, accurate material dosing, mechanization and miniaturization of the soldering procedure. Naturally, additional requirements are imposed on the particle size in powder solders.

The rejection of the solder based on Sn–38.1wt%Pb eutectic alloy (T_m 183 °C) use and intensive search for alternative tin-containing solders with low melting point began after the adoption of the Directive 2002/96/EC on Waste Electrical and Electronic Equipment (WEEE) by the European Parliament and the Council in 2003 [1, 2]. Sn–0.7wt%Cu (T_m 227 °C), Sn–3.5wt% Ag (T_m 221 °C), Sn–8.8wt%Zn (T_m 198.5 °C), Sn–57wt%Bi (T_m 139 °C), Sn–51.7wt%In (T_m 120 °C) eutectic alloys as well as a number of multicomponent alloys based on tin, silver, copper, zinc, bismuth and indium proved to be the most demanded among the founded candidates [2, 3]. Sn–8.8wt%Zn eutectic alloy has a special place among them since it is cheaper and has good mechanical properties although it is inferior to Sn–57wt%Bi and Sn–51.7wt%In alloys in melting point. However, the practical use of this alloy as a solder in its pure form is hindered by tin and zinc oxidation during crystallization and existence in eutectic phase since intermetallic compounds are not formed in Sn–Zn binary system.

To overcome this problem the alloying metals such as copper, nickel, silver, antimony or bismuth are added to the solder. Nickel is considered to be most suitable alloying metal since stable binary intermetallic compounds are formed in Ni–Zn system. They improve the wettability with Sn–8.8wt%Zn alloy of nickel coatings which are widely used as a diffusion barrier in electronics [4]. Moreover, the addition of nickel can lead to the formation of ternary intermetallic compounds and, consequently, it can improve mechanical properties and corrosion resistance of the joint [5].

In this regard, some methods of Zn–Sn–Ni ternary alloy coatings deposition have been developed. These coatings are

characterized by higher corrosion resistance, excellent solderability and electrical conductivity in comparison with coatings based on Sn–Zn and Ni–Zn binary alloys [6, 7]. As for Zn–Sn–Ni powder alloy, there is no information on its preparation and properties in the literature.

Different researchers have mainly studied the phase equilibria in this ternary system at various temperatures [8–10] as well as the crystal structures of ternary intermetallic compounds formed during heating [11]. This information is important for understanding the processes occurring at the interface “solder Sn–8.8wt%Zn – nickel substrate” during the formation of soldered joint. The principal possibility of Zn–Sn–Ni alloy application as a high-temperature solder is only noted. It is supposed that on purpose to reduce the melting point it is necessary to obtain an alloy with high tin and low nickel content.

In industry powder solders are mainly obtained by dispersion of pure metallurgical bars or spraying of melts with gas or high pressure water steam. However, these methods are material- and energy-intensive. Therefore the actual task is to search and develop simpler, less expensive, materials saving and low-temperature methods of powder materials production which are not inferior to industrial analogues in quality. Cementation processes are one of such methods. They are widely used in hydrometallurgical recovery of metals from solutions and purification of technological solutions and industrial effluents from metal ions, especially heavy ones [12]. Cementation reactions are characterized by high process rates and implementation simplicity. However, cementation has not yet found wide industrial application as a method of powder materials obtaining. Firstly, it is difficult to control chemical composition and particle size of the resulting powder product because of high process rates. Secondly, the additional purification (washing) of powders obtained by cementation from solution components is required in contrast to metallurgical methods.

The rate of cementation depends on many factors, which include solution concentration, pH and temperature, organic substances additives such as surfactants, cementing metal nature, process duration, stirring speed. On the one hand, the diversity of these factors provides difficulties in control of powder products composition. But thanks to these factors the possibilities of powders composition variation are opened up. The cementation processes advantage is the possibility of low-temperature alloy formation which already proceeds during the reduction of metal ions from solutions [13].

The purpose of this work was to develop a method of Zn–Sn–Ni powder obtaining by cementation of Ni(II) and Sn(II) with zinc from solutions, to study its phase composition and phase transformations during heat treatment.

2. Experimental procedure

Sn–Ni–Zn ternary powder alloy was obtained by two-stage synthesis providing metals ratio control [14]. At the first stage Ni(II) ions were reduced with zinc powder from aqueous solution containing 0.42 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at $\text{Ni}^{2+} : \text{Zn}$ molar ratio equal to 1 : 1, pH 1.2, 50 °C and stirring. As a result, Ni–Zn powder formation of “zinc core – nickel shell” type occurred.

After thorough washing with distilled water the obtained powder was filtered and placed in aqueous solution (pH 1.2) containing 0.05 M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The second step of synthesis (tin deposition) from this solution was also carried out at 50 °C and stirring. The deposition of external tin layer on Ni–Zn core with the formation of Sn–Ni–Zn powder was initiated by zinc remained after the first stage of synthesis. We varied the duration of Ni(II) reduction with zinc (t_{Ni}) from 30 s to 20 min at fixed time of tin deposition on Ni–Zn core ($t_{\text{Sn}} = 10$ min). The duration of tin deposition on this core was also varied from 30 s to 20 min at the specified $t_{\text{Ni}} = 3$ min. The resulting Sn–Ni–Zn powders were thoroughly washed with distilled water, filtered and dried to constant weight. A low pH value of solutions was necessary to prevent hydrolysis of Ni(II) and especially Sn(II) compounds.

The elemental composition of the powders was determined by energy dispersive X-ray microanalysis (EDX) using attachment (Rontec) to the scanning electron microscope (LEO 1420, Germany). The probing depth was about 2 μm .

The powders obtained were pressed into tablets with diameter of 1 cm by cold pressing under the pressure of about 2721 $\text{t} \cdot \text{m}^{-2}$ for efficient proceeding of phase transformations during their heat treatment.

The phase composition of the samples was studied by X-ray phase analysis (XRD) using X-ray diffractometer (DRON-3.0, Russia). XRD patterns were recorded at the rate of one degree per minute using $\text{CoK}\alpha$ radiation ($\lambda = 1.78897 \text{ \AA}$). The position of the analyzed lines maxima in XRD patterns was measured with an accuracy of ± 0.01 degrees. The lines were identified using JCPDS card files.

The behavior of the samples during heating was studied in the temperature range of 30–400 °C by differential scanning calorimetry (DSC) method with NETZSCH STA 449 F3 Jupiter (Germany). Heating was carried out in nitrogen atmosphere at the rate of 10 $\text{K} \cdot \text{min}^{-1}$.

To study phase transformations the tablets were heated for 3 h in a tube-type furnace in argon atmosphere at 260 °C. The temperature choice was based on the data in the work [15] where the formation of triple intermetallic phases at stated temperature was observed in the study of Sn–Zn–Ni alloys obtained from metallurgical metal powders.

3. Results and discussion

The effect of t_{Ni} time at fixed t_{Sn} value (10 min) on the elemental composition of Sn–Ni–Zn powders obtained is illustrated by EDX analysis data presented in Table 1.

Table 1. Metal content change (± 5 at. %) in Sn–Ni–Zn powders depending on t_{Ni} ($t_{\text{Sn}} = 10$ min) and t_{Sn} ($t_{\text{Ni}} = 3$ min)

Metal	t_{Ni} (min) at $t_{\text{Sn}} = 10$ min				t_{Sn} (min) at $t_{\text{Ni}} = 3$ min			
	0,5	5	10	20	0,5	5	10	20
Ni	38	67	62	86	50	43	44	47
Sn	38	23	30	7	34	40	41	34
Zn	24	10	8	7	16	17	15	19

It can be seen that an increase in t_{Ni} from 30 s to 20 min provides the growth of nickel content in the powders from 38 to 86 at. %, herewith zinc and tin percentages decrease from 24 to 7 at. % and from 38 to 7 at. % accordingly. The change in tin and nickel content in the powders with t_{Ni} increase is not monotonous. This fact can be caused by reasons related to the mechanism of cementation reaction. They are changes in the area and structure of

the reaction front, the decrease in the area of zinc microanodes and the rise of diffusion difficulties and ohmic losses in the pores of nickel shell which contain solution.

The variation of tin deposition duration at fixed time of nickel cementation (3 min) caused only slight change in content of this metal (within 34–41 at. %). This fact can indicate that the area of microanodes in Ni–Zn core is limited and rapidly decreases.

From the data in Table 1 it follows that in order to obtain Sn–Ni–Zn powders with high tin quota (30–40 at. %) it is necessary to carry out synthesis at minor t_{Ni} time (up to 10 min).

XRD analysis of freshly obtained samples with high tin content (for example, $\text{Sn}_{41}\text{Ni}_{44}\text{Zn}_{15}$ powders) shows the availability of β -Sn crystalline phase (intense peaks) together with NiZn_3 and NiSn intermetallic compounds (Fig. 1a). Note, that NiSn phase is absent on the equilibrium state diagram of Sn–Ni system [16].

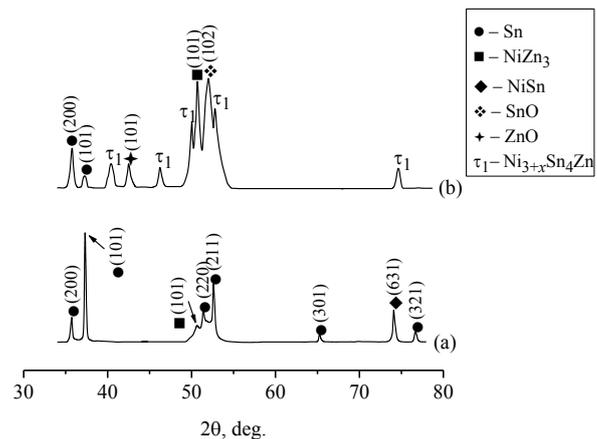


Fig. 1. XRD patterns of tablets made from $\text{Sn}_{41}\text{Ni}_{44}\text{Zn}_{15}$ powders: freshly obtained (a) and heated at 260 °C for 3 h (b).

The broadening of phase reflections in XRD patterns in the range of 2θ angles about 50–54 degrees can indicate their amorphous state. Note, that nickel is often deposited from solutions in amorphous or poorly crystallized state. The reflections of Zn phase are not clearly expressed in XRD patterns. That is due to shielding of zinc core with nickel and tin shells formed successively.

As mentioned above, Sn–Ni–Zn powders can be of interest in soldering processes, and therefore information on their thermal behavior at heating is needed. The results of thermal analysis of tablets pressed from $\text{Sn}_{41}\text{Ni}_{44}\text{Zn}_{15}$ powders before and after their heat treatment are shown in Fig. 2.

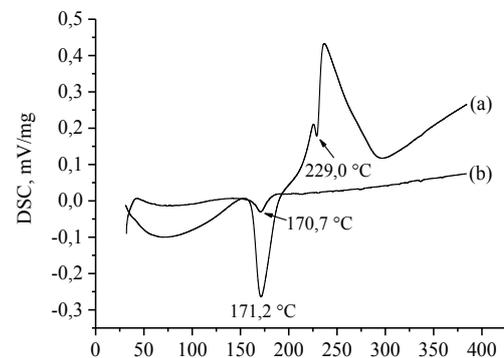


Fig. 2. DSC curves illustrating thermal behavior of tablets pressed from $\text{Sn}_{41}\text{Ni}_{44}\text{Zn}_{15}$ powders: freshly obtained (a) and heated at 260 °C for 3 h (b)

Two endothermic peaks are observed on DSC curve during heating of freshly obtained samples (Fig. 2a). One quite intense peak with a maximum at the temperature of about 171 °C can indicate the melting of Sn–Zn eutectic. The temperature of the end of this peak coincides with the reference data on the melting point

of Sn–Zn eutectic. The shift of the peak to lower temperatures as compared with the melting point of the eutectic can be caused by ultrafine state of the resulting powders [14]. One more endothermic peak is observed at the temperature of 229 °C. This peak can arise owing to melting of metallic tin, the presence of which was proved by XRD data. It is worth noting that in case of Sn–Ni–Zn powders with low tin content (up to 30 at. %) obtained at $t_{Ni} > 10$ min these peaks on DSC curves are of extremely low-intensity or completely absent.

There is a broad exothermic peak on the DSC curve of freshly obtained $Sn_{41}Ni_{44}Zn_{15}$ powders in the region of 230–300 °C (Fig. 2a). Its appearance can indicate the formation of intermetallic compounds during heating of samples above the melting point of tin. Indeed, XRD pattern reveals peaks of τ_1 ternary intermetallic phase (Fig. 1b) after heating of tablets at 260 °C for 3 h. $Ni_{3+x}Sn_4Zn$ composition is attributed to this phase [11]. Chen et al. [15] have also discovered τ_1 -phase during the heating at 250 °C of metallurgical powder mixtures with the composition close to the composition of the samples we studied. Since there is no XRD data in JCPDS on ternary intermetallic compounds in Sn–Ni–Zn system the values of interplanar spacing (d_{lit}) obtained by the authors of [9] were used as reference data to confirm the presence of τ_1 -phase in the heated samples. In turn, we calculated d_{calc} from the experimental values of $2\theta_{exp}$ angles corresponding to the assumed τ_1 -phase reflections using the Bragg's law and compared with d_{lit} . The calculation results are shown in Table 2.

Table 2. The values of interplanar spacing corresponding to τ_1 -phase calculated from XRD experimental data and published in [9]

$2\theta_{exp}$, deg	d_{calc} , Å	d_{lit} , Å [9]
40,403	2,59	2,59
46,237	2,28	2,28
50,036	2,11	2,11
52,790	2,01	2,01
74,640	1,47	1,46

As can be seen from Table 2 the complete coincidence of interplanar spacing values confirms our assumptions about the correspondence of some reflections in XRD pattern of the heated samples to τ_1 -phase. At the same time $2\theta_{exp}$ experimental values shown in Table 2 do not coincide with the data given in JCPDS for individual phases of nickel, tin, and zinc as well as binary intermetallic compounds and oxide phases based on them that eliminates the correlation of the detected reflections to these phases.

The study of thermal behavior of tablets heated at 260 °C showed that an endothermic peak of tin melting is absent on DSC curve of these samples (Fig. 2b) and the intensity of Sn–Zn eutectic melting peak is significantly reduced compared to the same peak on DSC curve of freshly obtained sample (Fig. 2a). These data indicate that during heating of tablets at 260 °C most quantity of Sn–Zn eutectic and metallic tin completely were melted and consumed in the process of ternary intermetallic compound (τ_1) formation. Melting processes are not observed during the repeated heat treatment of these samples. This is very important for resoldering processes since the formed soldered joint will not melt during subsequent technological operations in this case.

The low-temperature phase transformation at 260 °C discovered by us as well as some researchers [8, 15] is undoubtedly of interest in soldering technology taking into account the perspective of Sn–Ni–Zn powder alloy use as a high-temperature solder. Unlike published works our powders were synthesized from solutions by simple and low-cost method. Their ultrafine state provided a slight reduction of melting point in case of Sn–Zn eutectic.

4. Conclusions

The low-temperature method of Sn–Ni–Zn powders synthesis by successive cementation of Ni(II) and Sn(II) with zinc powder from acidic solutions and the formation of “zinc core – porous nickel shell – external tin layer” structures has been proposed. The method provides metals ratio control in wide ranges by variation of

the process duration. The possibility to obtain Sn–Ni–Zn powders containing 7–41 at. % of tin, 37–87 at. % of nickel and 7–24 at. % of zinc has been revealed. It has been shown that cementation process provides to obtain not only individual metals (nickel and tin) but also binary alloys of these metals with zinc. Sn–Ni–Zn powders with a high tin quota (30–40 at. %) contain β -Sn and Zn phases, $NiZn_3$ and $NiSn$ intermetallics as well as Sn–Zn eutectic with the melting point (171 °C) less than the reference value (198.5 °C). The formation of the ternary intermetallic τ_1 -phase ($Ni_{3+x}Sn_4Zn$) occurs as a result of the powders heating at 260 °C. The discovered low-temperature phase transformation in Sn–Ni–Zn system at 260 °C is of interest for electronic equipment assembly processes that include consecutive stages of soldering and resoldering. This transformation is necessary to preserve soldered joints during subsequent heat treatments.

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References

- [1] G. Humpston, Principles of soldering, Ohio, ASM International, 2004.
- [2] Lead-free soldering in electronics: science, technology, and environmental impact, ed. by K. Sukanuma, New York, Marcel Dekker, Inc., 2004.
- [3] S.-W. Chen, Phase diagrams of Pb-free solders and their related materials systems, In: Lead-free electronic solders: A special issue of the Journal of Materials Science: materials in electronics systems, 2007.
- [4] W. Zhu, Interfacial reactions between Sn–Zn alloys and Ni substrates, J. Electron. Mater. (2010), 39(2): 209.
- [5] A.K. Gain, Effect of nano Ni additions on the structure and properties of Sn–9Zn and Sn–Zn–3Bi solders in Au/Ni/Cu ball grid array packages, Mater. Sci. Eng. B (2009), 162(2): 92.
- [6] S. Fashu, Electrodeposition of ternary Zn–Ni–Sn alloys from an ionic liquid based on choline chloride and their characterisation, Transactions of the IMF (2016), 94(5): 237.
- [7] K. Ishizuka, SOC-free, Zn–Sn–Ni-alloy-coated steel sheets for electronic devices, Nippon Steel & Sumitomo Metal technical report no. 108 (2015): 47.
- [8] J. Chang, Phase equilibria in the Sn–Ni–Zn ternary system: isothermal sections at 200 °C, 500 °C, and 800 °C, J. Electron. Mater. (2010), 39(12): 2643.
- [9] V. Gandova, Phase equilibria in the Sn–Zn–Ni system, Int. J. Mat. Res. (2011), 102(3): 257.
- [10] C. Schmetterer, The high-temperature phase equilibria of the Ni–Sn–Zn system: isothermal sections, Intermetallics (2011), 19(10): 1489.
- [11] C. Schmetterer, The crystal structures of $Ni_{3+x}Sn_4Zn$ and $Ni_{6+x}Sn_8Zn$ and their structural relations to $Ni_{3+x}Sn_4$, $NiSn$ and $Ni_{5-\delta}ZnSn_4$, J. Solid State Chem. (2016), 238: 139.
- [12] M.L. Free, Hydrometallurgy. Fundamentals and application, Hoboken, John Wiley & Sons, Inc., 2013.
- [13] T.N. Vorobyova, Chemical synthesis of Cu–Sn powder by tin(II) cementation with copper in aqueous solution, Surfaces and interfaces (2016), 4: 9.
- [14] O.N. Vrublevskaia, Synthesis of powders and coatings of tin and its alloys with a controlled composition and structure by cementation from solutions, In: Advances in Chemistry Research, vol. 52, New York, Nova Science Publishers, Inc., 2019.
- [15] S.-W. Chen, Isothermal section of ternary Sn–Zn–Ni phase equilibria at 250 °C, Prog. Nat. Sci.: Mat. Int. (2011), 21(5): 386.
- [16] H. Okamoto, Ni–Sn (Nickel–Tin), J. Phase Equil. Dif. (2008), 29(3): 297.