**ABSTRACT:** Heat effects for the addition of Co in bulk and nanosized forms into the liquid Sn-3.8Ag-0.7Cu alloy were studied using drop calorimetry at four temperatures between 673 and 1173 K. Significant differences in the heat effects between nano and bulk Co additions were observed. The considerably more exothermic values of the measured enthalpy for nano Co additions are connected with the loss of the surface enthalpy of the nanoparticles due to the elimination of the surface of the nanoparticles upon their dissolution in the liquid alloy. This effect is shown to be independent of the calorimeter temperature (it depends only on the dropping temperature through the temperature dependence of the surface energy of the nanoparticles). Integral and partial enthalpies of mixing for Co in the liquid SAC-alloy were evaluated from the experimental data.

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**1. INTRODUCTION**

Unique physical–chemical properties and microstructure features make Sn–Ag–Cu (SAC) alloys the worldwide most used lead-free solders. In particular, the Sn-based Sn-3.8Ag-0.7Cu (wt %) alloy (SAC387), which corresponds to Sn-4.1Ag-1.3Cu (at. %), is employed extensively in the modern electronics industry. However, two main problems caused by using such type of lead-free solder are still not solved (i.e., the much higher melting temperature compared to traditional lead-containing solders and the extensive growth of brittle intermetallic layers). During the past decade, many attempts were made to decrease the melting temperature of lead-free solders and improve the mechanical reliability of the corresponding solder joints.

One of the most popular ways to achieve such improvements is the addition of a fourth element. According to investigations of the mechanical and thermodynamic properties and the microstructure, minor doping of active nanoparticles should be a promising solution of the above-mentioned problems.

Different heat effects are expected for the addition of Co in bulk and nanosized form into the liquid SAC387 alloy, and this difference is caused by the surface enthalpy of the nanoparticles. A number of studies have been dedicated to the investigations of the heat effects caused by the surface enthalpy of nanoparticles. However, most of these describe the heat effects for ceramic nanoparticles and/or are theoretical estimates.

The purpose of the present work is to provide experimental heat effect data for the addition of Co in bulk and nanosized form into the liquid SAC387 alloy using drop calorimetry. The integral and partial enthalpies of mixing for the quaternary Ag–Co–Cu–Sn system in the Sn-rich corner are estimated. At the same time, calculations are performed to predict the expected differences in the data obtained for bulk and nanosized Co caused by the surface enthalpy of Co nanoparticles.

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**2. EXPERIMENTAL DETAILS**

The calorimetric measurements were carried out using a Calvet-type twin microcalorimeter system, based on a commercial wire wound resistance furnace (HTC-1000, SETARAM, Lyon, France) having two thermopiles with more than 200 thermocouples, equipped with a self-made automatic drop device for up to 30 drops; control and data evaluation were performed with Lab View and HiQ. This system was described in detail by Flandorfer et al. The measurements were performed in BN crucibles under Ar flow (99.999 vol %, purification from oxygen, approximately 30 mL/min). At the end of each series, the calorimeter was calibrated by five drops of standard α-Al₂O₃ provided by NIST (National Institute of Standards and Technology, Gaithersburg, MD). The time interval between individual drops was usually 40 min, and the acquisition interval of the heat flow was 0.5 s. The obtained signals were recorded and integrated. The measured enthalpy (integrated heat flow at constant pressure) is

\[ \Delta H_{\text{signal}} = n_i \left( \Delta H_{\text{signal}}^i \right) = n_i \left( H_{m,i,T_a} - H_{m,i,T_f} \right) + \Delta H \]

(1)
Table 1A. Enthalpies of Mixing Data for the Addition of Bulk Co into the Liquid Sn–4.1Ag–1.3Cu Alloy; Standard States: Pure Liquid Metals; Values in Bold Font Refer to Liquid–Solid Two–State Region

| $n_{Co}$ (10^{-3} mol) | $\Delta H_{mix,i}^a$ (J mol^{-1}) | $x_{Co}$i (at. %) | $\Delta_{mix,H_{mix}}$ (J mol^{-1}) | $\Delta_{mix,H}$ (J mol^{-1}) |
|------------------------|----------------------------------|-------------------|----------------------------------|----------------------------------|
| 1.0397                 | 29717                            | 0.0061            | −19550                           | 71                               |
| 1.1484                 | 29648                            | 0.0188            | −19619                           | −168                            |
| 1.2295                 | 29910                            | 0.0322            | −19357                           | 0.0212                           |
| 1.2441                 | 30055                            | 0.0458            | −19212                           | 0.0254                           |
| 1.3018                 | 30309                            | 0.0594            | −18958                           | 0.0391                           |
| 1.3480                 | 30208                            | 0.0731            | −19059                           | 0.0525                           |
| 1.3978                 | 30430                            | 0.0869            | −18837                           | 0.0662                           |
| 1.4419                 | 30261                            | 0.1008            | −19006                           | 0.0800                           |
| 1.5194                 | 30802                            | 0.1148            | −18465                           | 0.0939                           |
| 1.5253                 | 30774                            | 0.1288            | −18493                           | −1738                            |
| 1.5565                 | 30461                            | 0.1425            | −18806                           | −2002                            |
| 1.5776                 | 30153                            | 0.1559            | −19114                           | −2263                            |
| 1.7203                 | 29854                            | 0.1697            | −19414                           | −2518                            |
| 1.8087                 | 29325                            | 0.1839            | −19942                           | −3307                            |
| 1.9625                 | 29857                            | 0.1986            | −19411                           | −3596                            |

*Average of $x_{Co}$ before and after drop; $x^{b}_{Co}$ after drop

where $n_i$ is the number of moles of the added element $i$, $H_m$ denotes molar enthalpies, $T_D$ is the drop temperature, $\Delta H_{mix,i}^a$ is the measured enthalpy in J mol^{-1}, and $T_M$ is the calorimeter temperature of the respective measurement in Kelvin. The molar enthalpy difference ($H_{mix,T} - H_{mix,T_D}$) was calculated using the SGTE data for pure elements.20 Because of the rather small masses of added component $i$, partial enthalpies can be calculated directly as

$$\Delta_{mix,H} = \Delta H / n_i$$

The integral molar enthalpy of mixing, $\Delta_{mix,H}$, was calculated by summing the respective reaction enthalpies and division by the total molar amount of substance, where $n_j$ stands for the molar amount of substance which was already present in the crucible:

$$\Delta_{mix,H} = \sum \Delta H / \sum n_i$$

Pure metals of high purity (99.99%, Alfa Aesar, Karlsruhe, Germany) were used without further purification as well as commercial nanosized Co (99.9%, average particle size 28 nm, IoLiTec Nanomaterials, Heilbronn, Germany). According to the technical data sheet,21 the BET surface area of the nanosized Co particles was about $A_{BET} = (50 \pm 10) \times 10^3$ m^2 kg^{-1}. The SAC387 alloys were prepared from pure components sealed in quartz ampoules and kept in the furnace at 1173 K for 2 weeks. All operations with nano Co were performed in a glovebox (M.Braun, LabMaster 130) in an atmosphere of purified Ar (O_2 and H_2O < 5 ppm each). The calorimetric measurements were carried out by the addition of solid Co in bulk and nanosized form into liquid SAC387 alloys at four different temperatures from 673 to 1173 K. In the second case, Co nanoparticles were first packed into a SAC387 foil with a thickness of about 50 µm which had been formed using a foil rolling mill. The measurements with additions of packed nano Co were started by dropping five pieces of SAC387 foil in order to determine and, subsequently, subtract the heat effect of the

| $n_{Co}$ (10^{-3} mol) | $\Delta H_{mix,i}^a$ (J mol^{-1}) | $x_{Co}$i (at. %) | $\Delta_{mix,H_{mix}}$ (J mol^{-1}) | $\Delta_{mix,H}$ (J mol^{-1}) |
|------------------------|----------------------------------|-------------------|----------------------------------|----------------------------------|
| 0.3905                 | 22407                            | 0.0045            | −23751                           | 0.0991                           |
| 0.4952                 | 22988                            | 0.0147            | −23170                           | 0.0204                           |
| 0.4959                 | 23166                            | 0.0259            | −22992                           | 0.0315                           |
| 0.5064                 | 23313                            | 0.0370            | −22844                           | 0.0425                           |
| 0.5216                 | 24022                            | 0.0481            | −22135                           | 0.0536                           |
| 0.5404                 | 24058                            | 0.0592            | −22099                           | 0.0649                           |
| 0.5430                 | 24322                            | 0.0704            | −21836                           | 0.0759                           |
| 0.5503                 | 23879                            | 0.0814            | −22279                           | 0.0868                           |
| 0.5874                 | 24786                            | 0.0925            | −21371                           | 0.0982                           |
| 0.5927                 | 24008                            | 0.1038            | −22149                           | 0.1094                           |
| 0.6270                 | 24938                            | 0.1151            | −21219                           | 0.1209                           |
| 0.6668                 | 25388                            | 0.1269            | −20769                           | 0.1329                           |
| 0.6822                 | 25189                            | 0.1388            | −20968                           | 0.1448                           |
| 0.6937                 | 25524                            | 0.1506            | −20633                           | 0.1565                           |
| 0.7101                 | 25931                            | 0.1623            | −20226                           | 0.1681                           |
| 0.7094                 | 25903                            | 0.1738            | −21064                           | 0.1795                           |
| 0.7411                 | 25737                            | 0.1853            | −20421                           | 0.1910                           |
| 0.7433                 | 24797                            | 0.1967            | −21410                           | 0.2023                           |
| 0.7859                 | 25706                            | 0.2081            | −20451                           | 0.2139                           |
| 0.7904                 | 25082                            | 0.2196            | −21075                           | 0.2252                           |
| 0.8096                 | 24683                            | 0.2309            | −21474                           | 0.2365                           |
| 0.8790                 | 25622                            | 0.2424            | −20535                           | 0.2483                           |
| 0.9115                 | 25117                            | 0.2543            | −21040                           | 0.2603                           |
| 0.9201                 | 25341                            | 0.2661            | −20816                           | 0.2719                           |
| 1.0400                 | 25304                            | 0.2783            | −20853                           | 0.2846                           |

*Average of $x_{Co}$ before and after drop; $x^{b}_{Co}$ after drop
Table 1C. Enthalpies of Mixing Data for the Addition of Bulk Co into the Liquid Sn—4.1Ag—1.3Cu Alloy; Standard States: Pure Liquid Metals; Values in Bold Font Refer to Liquid—Solid Two—State Region

| mol Co dropped | measured enthalpy | partial molar enthalpy | integral molar enthalpy |
|----------------|-------------------|------------------------|-------------------------|
| n_Co (10^{-3} mol) | ΔH_{mix} (J mol^{-1}) | x_Co | ΔH_{vap} (J mol^{-1}) | x_Co | ΔH_{mix} (J mol^{-1}) |
| 0.1237 | 22134 | 0.0014 | −24049 | 0.0028 | 24 |
| 0.1946 | 22496 | 0.0049 | −23686 | 0.0071 | −78 |
| 0.2023 | 21999 | 0.0093 | −24184 | 0.0115 | −186 |
| 0.2372 | 22198 | 0.0141 | −23985 | 0.0166 | −310 |
| 0.2456 | 22835 | 0.0193 | −23347 | 0.0219 | −433 |
| 0.2786 | 22815 | 0.0248 | −23368 | 0.0278 | −571 |
| 0.2912 | 22842 | 0.0308 | −23340 | 0.0338 | −713 |
| 0.2998 | 22979 | 0.0369 | −23203 | 0.0400 | −856 |
| 0.3484 | 23528 | 0.0435 | −22654 | 0.0470 | −1016 |
| 0.4206 | 24054 | 0.0512 | −22129 | 0.0554 | −1201 |
| 0.4108 | 23968 | 0.0594 | −22214 | 0.0634 | −1379 |
| 0.4444 | 24200 | 0.0676 | −21983 | 0.0719 | −1566 |
| 0.4707 | 24095 | 0.0763 | −22087 | 0.0807 | −1761 |
| 0.4761 | 23903 | 0.0850 | −22279 | 0.0894 | −1955 |
| 0.4799 | 24240 | 0.0937 | −21763 | 0.0980 | −2142 |
| 0.5187 | 24391 | 0.1025 | −21791 | 0.1071 | −2340 |
| 0.6405 | 24739 | 0.1126 | −21443 | 0.1181 | −2576 |
| 0.6338 | 24509 | 0.1234 | −21674 | 0.1287 | −2804 |
| 0.7477 | 24354 | 0.1346 | −21829 | 0.1406 | −3065 |

Average of x_Co before and after drop; x_Co after drop

SAC387 foil from the obtained measured enthalpy. To prove the accuracy of this procedure, we also performed a few measurements by packing bulk Co into the SAC387 foil. For instance, the second measurement runs at 1073 and 873 K were performed in such a way. The starting values of ΔH_{mix} for the ternary Ag—Cu—Sn subsystem required for the evaluation of the integral molar enthalpy of mixing for quaternary liquid Ag—Co—Cu—Sn alloys were calculated by a Redlich–Kister–Muggianu polynomial using experimental data taken from Luef et al. 22

Random as well as systematic errors of drop calorimetry depend on the calorimeter construction, calibration procedure, signal integration, and “chemical errors”, for example, incomplete reaction or impurities. Considering many calibration measurements done by dropping NIST standard sapphire, the standard deviation can be estimated to be less than ±1%. The systematic errors are mainly caused by parasitic heat flows, baseline problems at signal integration, and dropping and mixing problems. One can estimate that the random error of the measured enthalpy is ±150 J.

Selected furnace-cooled alloys after calorimetric runs were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD) to check for complete dissolution of the dropped component. The powder XRD measurements were done on a Bruker D8 diffractometer at ambient temperature using Ni-filtered Cu Kα radiation (accelerating voltage 40 kV, electron current 40 mA). The diffractometer operates in the 0/2θ mode. The powder was fixed with petroleum jelly on a single crystal silicon sample carrier which was rotated during the measurement. The detection unit was a Lynxeye strip

Table 1D. Enthalpies of Mixing Data for the Addition of Bulk Co into the Liquid Sn—4.1Ag—1.3Cu Alloy; Standard States: Pure Liquid Metals; Values in Bold Font Refer to Liquid—Solid Two—State Region

| mol Co dropped | measured enthalpy | partial molar enthalpy | integral molar enthalpy |
|----------------|-------------------|------------------------|-------------------------|
| n_Co (10^{-3} mol) | ΔH_{mix} (J mol^{-1}) | x_Co | ΔH_{vap} (J mol^{-1}) | x_Co | ΔH_{mix} (J mol^{-1}) |
| 0.1103 | 12678 | 0.0007 | −27198 | 0.0014 | 113 |
| 0.1603 | 12460 | 0.0022 | −27416 | 0.0031 | 66 |
| 0.1670 | 12315 | 0.0040 | −27561 | 0.0048 | 17 |
| 0.1686 | 13049 | 0.0057 | −26827 | 0.0066 | −31 |
| 0.1697 | 12628 | 0.0075 | −27248 | 0.0084 | −80 |
| 0.1808 | 12417 | 0.0094 | −27459 | 0.0103 | −133 |
| 0.1863 | 12657 | 0.0113 | −27219 | 0.0123 | −186 |
| 0.2004 | 12782 | 0.0133 | −27094 | 0.0143 | −243 |
| 0.2009 | 13235 | 0.0154 | −26642 | 0.0164 | −299 |
| 0.2164 | 13704 | 0.0175 | −26173 | 0.0187 | −357 |
| 0.2170 | 13992 | 0.0198 | −25885 | 0.0209 | −415 |
| 0.2513 | 14338 | 0.0222 | −25538 | 0.0235 | −481 |
| 0.2524 | 14115 | 0.0247 | −25762 | 0.0260 | −548 |
| 0.2579 | 14328 | 0.0273 | −25548 | 0.0286 | −615 |
| 0.2592 | 15007 | 0.0299 | −24870 | 0.0312 | −680 |
| 0.2649 | 14327 | 0.0326 | −25549 | 0.0339 | −748 |
| 0.2801 | 15543 | 0.0353 | −24333 | 0.0367 | −816 |
| 0.2865 | 14673 | 0.0381 | −25203 | 0.0395 | −888 |
| 0.2931 | 15663 | 0.0410 | −24213 | 0.0424 | −958 |
| 0.3008 | 15421 | 0.0439 | −24455 | 0.0453 | −1030 |
| 0.2997 | 14938 | 0.0468 | −24938 | 0.0482 | −1130 |
| 0.3067 | 15275 | 0.0497 | −24601 | 0.0512 | −1176 |
| 0.3288 | 14860 | 0.0528 | −25017 | 0.0544 | −1255 |
| 0.3338 | 16233 | 0.0560 | −23643 | 0.0575 | −1330 |
| 0.4503 | 15343 | 0.0597 | −24534 | 0.0618 | −1435 |

Average of x_Co before and after drop; x_Co after drop
detector. Indexing of the phases was supported by the Inorganic Crystal Structural Database (ICSD). Rietveld refinement of the XRD patterns was done with the Topas3 software provided by Bruker AXS.

The electron microscope Zeiss Supra 55 VP was used for metallographic investigations. The excitation energy of the electron beam was 15–20 kV; backscattered electrons were detected in order to visualize the surfaces of the samples. The chemical analyses of the sample phases were performed using the energy dispersive X-ray (EDX) technique with the two characteristic spectral lines of Cu (K-line) and Sn (L-line). Standard deviations for the chemical compositions obtained from EDX were about ±1 at%.

3. RESULTS AND DISCUSSION

The molar enthalpy data for the additions of bulk Co into the liquid SAC387 alloy are presented in Tables 1A–1G. Since the Co additions in this paper are presented in at. %, the composition of the SAC387 master alloy is also given in at. % (Sn-4.1Ag-1.3Cu) below. A kink in the concentration dependencies of the integral enthalpies of mixing as well as constant partial enthalpy values indicate the transition of the investigated state region.

Table 1E. Enthalpies of Mixing Data for the Addition of Bulk Co into the Liquid Sn–4.1Ag–1.3Cu Alloy; Standard States: Pure Liquid Metals; Values in Bold Font Refer to Liquid–Solid Two–State Region

| mol Co dropped \( n_{\text{Co}} \) (10\(^{-3}\) mol) | measured enthalpy \( \Delta H_{\text{pul}} \) (J mol\(^{-1}\)) | partial molar enthalpy \( x_{\text{Co}}^a \) (at. %) | integral molar enthalpy \( \Delta_{\text{mix}}H \) (J mol\(^{-1}\)) | integral molar enthalpy \( \Delta_{\text{mix}}H \) (J mol\(^{-1}\)) |
|-------------------------------------------------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 0.1717                                          | 12595                                           | 0.0009                          | −27256                          | 0.0018                          | 150                             |
| 0.1578                                          | 12641                                           | 0.0026                          | −27211                          | 0.0035                          | 55                              |
| 0.1178                                          | 12324                                           | 0.0041                          | −27527                          | 0.0047                          | 21                              |
| 0.1712                                          | 13503                                           | 0.0056                          | −26348                          | 0.0065                          | −26                             |
| 0.2830                                          | 13965                                           | 0.0079                          | −25887                          | 0.0094                          | −103                            |
| 0.2204                                          | 12976                                           | 0.0105                          | −26875                          | 0.0116                          | −164                            |
| 0.2047                                          | 12945                                           | 0.0127                          | −26906                          | 0.0137                          | −220                            |
| 0.1719                                          | 14368                                           | 0.0146                          | −25483                          | 0.0155                          | −265                            |
| 0.2965                                          | 14150                                           | 0.0169                          | −25702                          | 0.0184                          | −342                            |

\( ^a \)Average of \( x_{\text{Co}} \) before and after drop; \( ^b \) \( x_{\text{Co}} \) after drop

Table 1F. Enthalpies of Mixing Data for the Addition of Bulk Co into the Liquid Sn–4.1Ag–1.3Cu Alloy; Standard States: Pure Liquid Metals; Values in Bold Font Refer to Liquid–Solid Two–State Region

| mol Co dropped \( n_{\text{Co}} \) (10\(^{-3}\) mol) | measured enthalpy \( \Delta H_{\text{pul}} \) (J mol\(^{-1}\)) | partial molar enthalpy \( x_{\text{Co}}^a \) (at. %) | integral molar enthalpy \( \Delta_{\text{mix}}H \) (J mol\(^{-1}\)) | integral molar enthalpy \( \Delta_{\text{mix}}H \) (J mol\(^{-1}\)) |
|-------------------------------------------------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 0.1162                                          | 7236                                            | 0.0006                          | 26715                           | 0.0012                          | 214                             |
| 0.1653                                          | 7312                                            | 0.0021                          | −26638                          | 0.0029                          | 158                             |
| 0.1807                                          | 7211                                            | 0.0038                          | −26740                          | 0.0047                          | 109                             |
| 0.1816                                          | 7252                                            | 0.0056                          | −26699                          | 0.0066                          | 60                              |
| 0.1812                                          | 7931                                            | 0.0075                          | −26200                          | 0.0084                          | 12                               |
| 0.1937                                          | 7707                                            | 0.0093                          | −26243                          | 0.0103                          | −39                             |
| 0.2147                                          | 8337                                            | 0.0114                          | −25614                          | 0.0124                          | −94                             |
| 0.2155                                          | 7269                                            | 0.0135                          | −26882                          | 0.0146                          | −151                            |
| 0.2200                                          | 8147                                            | 0.0157                          | −25804                          | 0.0167                          | −208                            |
| 0.2185                                          | 8168                                            | 0.0178                          | −25782                          | 0.0189                          | −264                            |
| 0.2276                                          | 7937                                            | 0.0200                          | −26013                          | 0.0211                          | −322                            |
| 0.2415                                          | 8044                                            | 0.0223                          | −25446                          | 0.0235                          | −382                            |
| 0.2592                                          | 8186                                            | 0.0247                          | −25764                          | 0.0260                          | −447                            |
| 0.2791                                          | 9260                                            | 0.0273                          | −24691                          | 0.0286                          | −514                            |
| 0.2778                                          | 9706                                            | 0.0300                          | −24244                          | 0.0313                          | −579                            |
| 0.2887                                          | 9818                                            | 0.0327                          | −24133                          | 0.0340                          | −646                            |
| 0.2979                                          | 9164                                            | 0.0355                          | −24787                          | 0.0369                          | −716                            |
| 0.3231                                          | 9701                                            | 0.0384                          | −24250                          | 0.0399                          | −791                            |
| 0.3354                                          | 9818                                            | 0.0415                          | −24333                          | 0.0430                          | −867                            |
| 0.3889                                          | 9740                                            | 0.0448                          | −24211                          | 0.0466                          | −955                            |
| 0.4038                                          | 8487                                            | 0.0485                          | −25463                          | 0.0504                          | −1050                           |
| 0.4561                                          | 10152                                           | 0.0524                          | −23799                          | 0.0545                          | −1150                           |
| 0.5684                                          | 9480                                            | 0.0571                          | −24471                          | 0.0597                          | −1277                           |
| 0.6334                                          | 9904                                            | 0.0625                          | −24047                          | 0.0653                          | −1414                           |
| 0.8022                                          | 9839                                            | 0.0689                          | −24112                          | 0.0724                          | −1586                           |

\( ^a \)Average of \( x_{\text{Co}} \) before and after drop; \( ^b \) \( x_{\text{Co}} \) after drop
Table 1G. Enthalpies of Mixing Data for the Addition of Bulk Co into the Liquid Sn–4.1Ag–1.3Cu Alloy; Standard States: Pure Liquid Metals; Values in Bold Font Refer to Liquid–Solid Two–State Region

| mol Co dropped | measured enthalpy | partial molar enthalpy | integral molar enthalpy |
|----------------|------------------|------------------------|-------------------------|
| $n_{Co}$ (10$^{-3}$ mol) | $\Delta H_{mix}$ (J mol$^{-1}$) | $x_{Co}$ (at. %) | $\Delta H_{mix}^\Delta H_{Co}$ (J mol$^{-1}$) | $x_{Co}$ (at. %) | $\Delta H_{mix}^\Delta H_{mix}$ (J mol$^{-1}$) |
| 0.2751 | 8225 | 0.0032 | 25755 | 0.0065 | 79 |
| 0.3334 | 8133 | 0.0103 | 25847 | 0.0142 | 122 |
| 0.3972 | 8661 | 0.0187 | 25339 | 0.0232 | 353 |
| 0.2731 | 8970 | 0.0262 | 25009 | 0.0293 | 507 |
| 0.6589 | 8894 | 0.0333 | 25085 | 0.0372 | 708 |
| 0.108 | 9329 | 0.0406 | 24651 | 0.0440 | 875 |
| 0.2502 | 9542 | 0.0466 | 24438 | 0.0493 | 1008 |
| 0.4219 | 9639 | 0.0538 | 24340 | 0.0582 | 1226 |
| 0.6968 | 9798 | 0.0621 | 24181 | 0.0659 | 1413 |
| 0.4347 | 10190 | 0.0703 | 23790 | 0.0748 | 1626 |
| 0.4302 | 10403 | 0.0791 | 23576 | 0.0834 | 1830 |
| 0.5006 | 10038 | 0.0883 | 23942 | 0.0932 | 2067 |
| 0.4516 | 10247 | 0.0975 | 23733 | 0.1019 | 2274 |
| 0.3842 | 10499 | 0.1055 | 23481 | 0.1091 | 2445 |
| 0.5271 | 10174 | 0.1140 | 23805 | 0.1189 | 2679 |
| 0.5367 | 10279 | 0.1237 | 23700 | 0.1286 | 2911 |
| 0.4103 | 9977 | 0.1322 | 24002 | 0.1359 | 3088 |
| 0.6428 | 10103 | 0.1415 | 23877 | 0.1471 | 3357 |
| 0.5926 | 10329 | 0.1521 | 23651 | 0.1571 | 3596 |
| 0.7167 | 10000 | 0.1630 | 23799 | 0.1690 | 3882 |
| 0.7146 | 10048 | 0.1747 | 23931 | 0.1804 | 4159 |
| 0.7337 | 10208 | 0.1862 | 23771 | 0.1919 | 4433 |
| 0.6751 | 10360 | 0.1970 | 23619 | 0.2022 | 4677 |
| 0.7507 | 10104 | 0.2077 | 23876 | 0.2133 | 4945 |
| 0.7850 | 10364 | 0.2189 | 28530 | 0.2246 | 4996 |

*Average of $x_{Co}$ before and after drop; $b$x$_{Co}$ after drop.

Figure 1. Partial enthalpy of mixing of Co$_x$(Sn-4.1Ag-1.3Cu)$_{100-x}$ alloys (▲ = first measurement; red ▲ = second measurement) in comparison to Co$_x$Sn$_{100-x}$ alloys (○) at 873 K.\(^{23}\)

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were estimated at different temperatures. All values with the bold font in Tables 1A–1G refer to compositions outside the single-phase liquid state. It should also be noted that the obtained molar enthalpy data for quaternary Ag–Co–Cu–Sn alloys are practically identical to our recent data for the binary Co–Sn system.\(^{23}\) The difference between the partial enthalpies of mixing for the addition of bulk Co to liquid Sn and to the liquid Sn–4.1Ag–1.3Cu alloy does not exceed 1 kJ mol$^{-1}$ (cf. Figure 1). This is not surprising because of the high content of Sn in the SAC alloy.

It should be noted that in our measurements at 873 K, we observed an additional exothermic reaction immediately after the main endothermic reaction, whereas such effects were not observed at other temperatures. The total reaction time did not exceed 1500 s.

The resulting heat effects obtained for the addition of nanosized Co into the liquid Sn-4.1Ag-1.3Cu alloy show a marked difference compared to the values for bulk Co additions (Table 2A–2E). This difference is concentration independent.

Table 2A. Enthalpies of Mixing Data for the Addition of Nano Co into the Liquid Sn–4.1Ag–1.3Cu Alloy; Standard States: Pure Liquid Metals

| mol “nanosized” Co dropped | measured enthalpy | partial molar enthalpy | integral molar enthalpy |
|-----------------------------|------------------|------------------------|-------------------------|
| $n_{Co}$ (10$^{-3}$ mol) | $\Delta H_{mix}$ (J mol$^{-1}$) | $x_{Co}$ (at. %) | $\Delta H_{mix}^\Delta H_{Co}$ (J mol$^{-1}$) | $x_{Co}$ (at. %) | $\Delta H_{mix}^\Delta H_{mix}$ (J mol$^{-1}$) |
| 0.2355 | 20454 | 0.0026 | 21257 | 0.0051 | 38 |
| 0.2890 | 20273 | 0.0082 | 21439 | 0.0113 | 171 |
| 0.1514 | 20616 | 0.0129 | 21095 | 0.0145 | 239 |
| 0.1617 | 20589 | 0.0161 | 21122 | 0.0178 | 309 |
| 0.1676 | 20369 | 0.0195 | 21342 | 0.0212 | 382 |
| 0.1984 | 20120 | 0.0232 | 21592 | 0.0251 | 468 |
| 0.2029 | 20165 | 0.0271 | 21546 | 0.0291 | 555 |
| 0.1554 | 20766 | 0.0306 | 20945 | 0.0321 | 618 |
| 0.1447 | 21536 | 0.0335 | 20176 | 0.0348 | 673 |
| 0.1553 | 21004 | 0.0363 | 20707 | 0.0377 | 733 |
| 0.2231 | 20429 | 0.0398 | 21282 | 0.0419 | 822 |
| 0.1743 | 21924 | 0.0434 | 19787 | 0.0450 | 884 |
| 0.1924 | 21470 | 0.0467 | 20241 | 0.0484 | 954 |

*Average of $x_{Co}$ before and after drop; $b$x$_{Co}$ after drop.

at the investigated temperatures and is equal to $(-7.5 \pm 1.0) \times 10^3$ J mol$^{-1}$ (cf. Figure 2a–c). It should be also noted that the average error of estimated data for $\Delta H_{Signal}^b$ and $\Delta H_{mix}$ does not exceed 1000 J mol$^{-1}$.

The measured enthalpy ($\Delta H_{Signal}$) consists generally of two terms (see eq 1); however, we think that the additional heat effect resulting in less positive values of $\Delta H_{Signal}$ relates only to the first term of eq 1. The enthalpy of reaction ($\Delta H$) corresponds to the heat effects for interactions between atoms of the added component, i.e. liquid Co (remember that the standard state in Tables 1A–1G and Table 2A–2E is metastable liquid Co), and the liquid Sn-4.1Ag-1.3Cu alloy.

Therefore, this term should be the same independently whether Co is added in bulk or in nanoform. We suggest that this difference is caused by the excess enthalpy of the Co
The addition of nano Co can be rewritten as

\[ \Delta H_{\text{signal}} = \Delta H_{\text{signal}}^\text{Co} - \Delta H_{\text{signal}}^\text{bulk} \]

where \( \Delta H_{\text{signal}}^\text{Co} \) is the excess surface enthalpy of Co nanoparticles in J mol\(^{-1}\), which has a positive value. This additional term should be connected with the decrease in the melting temperature and latent heat of nanosized Co particles similarly to other metals in nanosized form.\(^{3,18,24}\) It is provided here with a negative sign (similar to \( H_{\text{mix, T}} \)), as the surface of the nanoparticles exists in these experiments only in the initial state.

Table 2B. Enthalpies of Mixing Data for the Addition of Nano Co into the Liquid Sn-4.1Ag-1.3Cu Alloy; Standard States: Pure Liquid Metals

| mol “nanized” Co dropped | measured enthalpy \( \Delta H_{\text{signal}} \) (J mol\(^{-1}\)) | partial molar enthalpy \( x_{C_{\text{co}}}a \) (at. %) | integral molar enthalpy \( \Delta_{\text{mix}}H \) (J mol\(^{-1}\)) |
|--------------------------|---------------------------------|-----------------|-----------------|
| \( n_{0.1140} \) (10\(^{-3}\) mol) | 13847 | 0.0013 | −24772 | 0.0026 | 26 ± 3 |
| \( 0.0721 \) | 12910 | 0.0034 | −25710 | 0.0042 | −16 ± 5 |
| \( 0.0740 \) | 13482 | 0.0050 | −25137 | 0.0059 | −57 ± 8 |
| \( 0.1094 \) | 14676 | 0.0115 | −23944 | 0.0127 | −224 |
| \( 0.1249 \) | 16532 | 0.0140 | −22087 | 0.0153 | −283 |
| \( 0.0596 \) | 14457 | 0.0160 | −2162 | 0.0166 | −314 |
| \( 0.0835 \) | 17940 | 0.0175 | −20679 | 0.0183 | −350 |
| \( 0.1006 \) | 15986 | 0.0194 | −22633 | 0.0204 | −398 |
| \( 0.0816 \) | 16097 | 0.0213 | −22522 | 0.0221 | −436 |
| \( 0.1710 \) | 17843 | 0.0239 | −20776 | 0.0256 | −509 |
| \( 0.1201 \) | 15868 | 0.0268 | −22752 | 0.0281 | −565 |
| \( 0.1133 \) | 16973 | 0.0292 | −21646 | 0.0303 | −613 |
| \( 0.0507 \) | 16427 | 0.0307 | −22192 | 0.0312 | −634 |

Table 2C. Enthalpies of Mixing Data for the Addition of Nano Co into the Liquid Sn-4.1Ag-1.3Cu Alloy; Standard States: Pure Liquid Metals

| mol “nanized” Co dropped | measured enthalpy \( \Delta H_{\text{signal}} \) (J mol\(^{-1}\)) | partial molar enthalpy \( x_{C_{\text{co}}}a \) (at. %) | integral molar enthalpy \( \Delta_{\text{mix}}H \) (J mol\(^{-1}\)) |
|--------------------------|---------------------------------|-----------------|-----------------|
| \( n_{0.0893} \) (10\(^{-3}\) mol) | 13905 | 0.0010 | −24715 | 0.0020 | 42 |
| \( 0.0809 \) | 15734 | 0.0028 | −22885 | 0.0037 | 1 |
| \( 0.0798 \) | 14076 | 0.0046 | −24544 | 0.0054 | −41 |
| \( 0.0619 \) | 15184 | 0.0061 | −23435 | 0.0067 | −72 |
| \( 0.0597 \) | 15532 | 0.0073 | −23087 | 0.0080 | −101 |
| \( 0.1223 \) | 16026 | 0.0092 | −22593 | 0.0105 | −159 |
| \( 0.0837 \) | 13970 | 0.0114 | −24649 | 0.0122 | −202 |
| \( 0.1150 \) | 15471 | 0.0134 | −23148 | 0.0146 | −257 |
| \( 0.1215 \) | 16197 | 0.0158 | −22422 | 0.0170 | −312 |
| \( 0.1210 \) | 13943 | 0.0182 | −24676 | 0.0194 | −371 |
| \( 0.1264 \) | 16626 | 0.0206 | −21993 | 0.0218 | −426 |
| \( 0.1429 \) | 14827 | 0.0232 | −23792 | 0.0246 | −492 |
| \( 0.1088 \) | 13268 | 0.0256 | −23531 | 0.0266 | −545 |
| \( 0.1020 \) | 14098 | 0.0276 | −24521 | 0.0285 | −592 |
| \( 0.1710 \) | 16393 | 0.0301 | −22227 | 0.0317 | −663 |
| \( 0.4397 \) | 16580 | 0.0358 | −22039 | 0.0399 | −843 |
| \( 0.1892 \) | 18417 | 0.0415 | −20202 | 0.0431 | −909 |

Average of \( x_{C_{\text{co}}} \) before and after drop; \( b x_{C_{\text{co}}} \) after drop.

It should be also noted that Table 2A–2E shows the recalculated molar enthalpies values including the excess enthalpy of Co nanoparticles term.

The partial and integral enthalpies of mixing, after taking into account the surface effect, are in good agreement. This is shown in Figure 3 where, as an example, the partial (Figure 3a) and integral enthalpies of mixing (Figure 3b) for additions of Co in bulk and nanized form at 1073 K are plotted as a function of the Co content.

Crossing the liquidus line into a two-phase field is usually indicated by a kink in the integral enthalpy of mixing and by constant values in the partial mixing enthalpy. The relatively small difference in the heat effects for minor additions of Co nanoparticles. Thus, the corresponding equation for \( \Delta H_{\text{signal}} \) for the addition of nano Co can be rewritten as

\[
\Delta H_{\text{signal}} = \Delta H_{\text{signal}}^\text{bulk} - \Delta H_{\text{signal}}^\text{ex}
\]

where \( \Delta H_{\text{signal}}^\text{ex} \) is the excess surface enthalpy of Co nanoparticles in J mol\(^{-1}\), which has a positive value. This additional term should be connected with the decrease in the melting temperature and latent heat of nanosized Co particles similarly to other metals in nanosized form.\(^{3,18,24}\) It is provided here with a negative sign (similar to \( H_{\text{mix, T}} \)), as the surface of the nanoparticles exists in these experiments only in the initial state.
Table 2D. Enthalpies of Mixing Data for the Addition of Nano Co into the Liquid Sn-4.1Ag-1.3Cu Alloy; Standard States: Pure Liquid Metals

| n<sub>Co</sub> (10<sup>-3</sup> mol) | measured enthalpy ΔH<sub>mix</sub><sup>a</sup> (J mol<sup>−1</sup>) | partial molar enthalpy x<sub>Co</sub><sup>a</sup> (at. %) | integral molar enthalpy Δ<sub>mix</sub> H (J mol<sup>−1</sup>) | T = 873 K; first measurement; starting amount: n<sub>Ag</sub> = 3.9667 × 10<sup>−3</sup> mol; n<sub>Cu</sub> = 1.2404 × 10<sup>−3</sup> mol; n<sub>Sn</sub> = 90.5884 × 10<sup>−3</sup> mol |
|---|---|---|---|---|
| 0.3341 | 5474 | 0.0017 | −26978 | 0.0035 | 150 |
| 0.2002 | 5889 | 0.0045 | −26564 | 0.0055 | 56 |
| 0.3014 | 6206 | 0.0070 | −26247 | 0.0085 | 1 |
| 0.2550 | 6117 | 0.0098 | −26335 | 0.0111 | −148 |
| 0.3680 | 6715 | 0.0129 | −25738 | 0.0147 | −243 |
| 0.2413 | 6506 | 0.0159 | −25946 | 0.0171 | −304 |
| 0.2579 | 6224 | 0.0183 | −26229 | 0.0195 | −370 |
| 0.4100 | 6809 | 0.0215 | −25643 | 0.0234 | −471 |
| 0.2713 | 7158 | 0.0247 | −25294 | 0.0259 | −535 |
| 0.1680 | 7386 | 0.0267 | −25066 | 0.0275 | −574 |
| 0.3068 | 7284 | 0.0289 | −25168 | 0.0303 | −645 |
| 0.3066 | 7196 | 0.0316 | −25256 | 0.0330 | −716 |
| 0.2079 | 7606 | 0.0339 | −24846 | 0.0348 | −761 |
| 0.2835 | 7208 | 0.0361 | −25244 | 0.0373 | −825 |

<sup>a</sup>Average of x<sub>Co</sub> before and after drop; <sup>b</sup>x<sub>Co</sub> after drop.

Table 2E. Enthalpies of Mixing Data for the Addition of Nano Co into the Liquid Sn-4.1Ag-1.3Cu Alloy; Standard States: Pure Liquid Metals

| n<sub>Co</sub> (10<sup>-3</sup> mol) | measured enthalpy ΔH<sub>mix</sub><sup>a</sup> (J mol<sup>−1</sup>) | partial molar enthalpy x<sub>Co</sub><sup>a</sup> (at. %) | integral molar enthalpy Δ<sub>mix</sub> H (J mol<sup>−1</sup>) | T = 873 K; second measurement; starting amount: n<sub>Ag</sub> = 4.0365 × 10<sup>−3</sup> mol; n<sub>Cu</sub> = 1.2622 × 10<sup>−3</sup> mol; n<sub>Sn</sub> = 92.1782 × 10<sup>−3</sup> mol |
|---|---|---|---|---|
| 0.4066 | 5492 | 0.0021 | −26985 | 0.0041 | 150 |
| 0.3933 | 4969 | 0.0061 | −27508 | 0.0081 | 37 |
| 0.3406 | 5628 | 0.0097 | −26849 | 0.0114 | −163 |
| 0.2384 | 5322 | 0.0126 | −27156 | 0.0137 | −226 |
| 0.3545 | 6575 | 0.0154 | −25902 | 0.0171 | −315 |
| 0.3477 | 7557 | 0.0187 | −24921 | 0.0204 | −398 |
| 0.2063 | 5470 | 0.0213 | −27007 | 0.0223 | −450 |
| 0.3867 | 7223 | 0.0241 | −25254 | 0.0258 | −541 |
| 0.4802 | 6574 | 0.0280 | −25904 | 0.0302 | −655 |
| 0.4334 | 7051 | 0.0321 | −25426 | 0.0341 | −754 |
| 0.4824 | 8586 | 0.0362 | −23892 | 0.0383 | −857 |
| 0.4315 | 6939 | 0.0402 | −25538 | 0.0421 | −953 |
| 0.4315 | 7846 | 0.0439 | −24631 | 0.0457 | −1044 |
| 0.2119 | 7299 | 0.0466 | −25178 | 0.0474 | −1087 |
| 0.2773 | 7041 | 0.0486 | −25436 | 0.0497 | −1145 |
| 0.3670 | 8884 | 0.0512 | −23593 | 0.0527 | −1216 |
| 0.4285 | 8910 | 0.0544 | −23567 | 0.0562 | −1299 |

<sup>a</sup>Average of x<sub>Co</sub> before and after drop; <sup>b</sup>x<sub>Co</sub> after drop.

both in the liquid and the semisolid Ag–Co–Cu–Sn alloys allows the estimation of the concentration of this transition only from the partial enthalpy of mixing data. These difficulties for the liquidus limit estimation were already pointed out for the investigation of the enthalpies of mixing in the binary Co–Sn system. The estimated limiting liquidus concentration values in the present study, approximately 2 at. % Co at 673 K, 4 at. % Co at 873 K, and 14 at. % Co at 1073 K are slightly larger (up to 1–2 at. %) than those for the binary Co–Sn system. However, it is still suggested that these transitions are connected with the precipitation of CoSn<sub>2</sub> (at 673 K) and CoSn (at 873 and 1073 K), in analogy to the corresponding binary phase diagram. In order to prove that all pieces of the solid component dropped into the liquid bath had completely dissolved, selected alloys were investigated by means of SEM-EDX and powder XRD measurements after the calorimeter had cooled. The results of phase analyses along with BSE images of two exemplary alloys can be found in Table 3. No residual pure Co was found in the investigated samples. However, even after slow cooling in the calorimeter, the samples are not in an equilibrium state. This is obvious by the presence of six different phases in a four-component system. Nevertheless, the absence of (Co) indicates full mixing and precipitation of Co-poor phases, either during measurement (beyond the liquidus limit) or during cooling after the measurement.
The XRD phase analysis fully confirmed the phases that had been found by SEM-EDX. Based on the SEM-EDX results Cu atoms replaced Co in the CoSn₃ compound, which was formed on cooling at 1226 ± 2 K.

4. THEORETICAL CONSIDERATIONS

In the present work, it is estimated that the term relating to the excess enthalpy of nanosized Co is practically the same for all investigated temperatures and equals to about (7.5 ± 1.0) · 10³ J·mol⁻¹. This term relates to the surface enthalpy of 1 mol of nanosized Co as

\[ \Delta H_{i, \text{surf}} = \Delta H_{i, \text{surf}} A_s \]  

where \( \Delta H_{i, \text{surf}} \) is the surface enthalpy in J m⁻² and \( A_s \) is the surface area for 1 mol of nanoparticles in the unit of m²·mol⁻¹. Assuming a strictly spherical shape of the nanoparticles, \( A_s \) can be expressed as

\[ A_s = 3 \frac{V_M}{r} = 3 \frac{M}{\rho r} \]  

where \( V_M \) is the molar volume; \( M \) is the molar mass; \( \rho \) is the density; and \( r \) is the radius of the particles. Inserting the corresponding values for Co, i.e. \( M = 58.933 \times 10^{-3} \) kg·mol⁻¹ and \( \rho = 8.890 \times 10^3 \) kg·m⁻³, and the radius of the Co nanoparticles (∼14 nm) results in a molar surface area of about 1.42 × 10⁵ m²·mol⁻¹. As mentioned above, the BET surface area of the Co nanopowder used here is equal to \( A_{\text{BET}} = (50 \pm 10)\times 10^3 \) m²·kg⁻¹ corresponding to \( A_s = (2.95 \pm 0.59) \times 10^3 \) m²·mol⁻¹. The obtained discrepancy between calculated and technical values is most probably caused by the variation in size (particle size range is given as 0–60 nm, with an average size of 28 nm) and shape of the employed nanoparticles; these values, in turn, combined with the experimental value of (7.5 ± 1.0) · 10³ J·mol⁻¹, give a surface enthalpy of about (2.85 ± 0.55) J·m⁻².

On the basis of the data presented above, it was decided to describe the observed phenomenon, related to the nano Co additions, according to the thermodynamic properties of nanosized particles. The molar enthalpy of nanoparticles can be expressed as

\[ \Delta H_{i, \text{nano}} = H_{i, \text{bulk}} + \Delta H_{\text{ex}} \]  

with

\[ \Delta H_{\text{ex}} = A_{\text{spec}} V_{M,T_0} \sigma_{g,H,T_0} \]  

where \( H_{i, \text{nano}} \) (J·mol⁻¹) is the molar enthalpy of the solid nanoparticles, \( H_{i, \text{bulk}} \) (J·mol⁻¹) is the molar enthalpy of the bulk solid; \( A_{\text{spec}} \) (m⁻¹) is the specific surface area of the nanoparticles defined as the ratio of their surface area to their volume, \( \sigma_{g,H,T_0} \) (J·m⁻²) is the enthalpy term of the surface energy of the solid nanoparticles at the dropping temperature. Although both molar volume and surface energy are T-dependent quantities, the total value of \( \Delta H_{\text{ex}} \) (as it is at the dropping temperature) is lost due to the elimination of the surface of the nanoparticles upon their dissolution in the liquid alloy, and therefore, the measured nanoheat-effect is not

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**Figure 2.** Concentration dependencies of the measured enthalpy at 1173 K (a), 1073 K (b) and 873 K (c) (□ – for additions of bulk Co; ■ – for additions of nanosized Co; red ▲ – after addition of the excess enthalpy term (7.5 × 10³ J·mol⁻¹) to \( \Delta H_{\text{surf}} \) for nanosized Co additions).

**Figure 3.** Partial (a) and integral (b) enthalpies of mixing of liquid Sn-4.1Ag-1.3Cu₁₀₀₋ₓCoₓ alloys (■ – bulk Co (first measurement); green ■ – bulk Co (second measurement); red ▲ – nano Co (first measurement, recalculated); Δ – nano Co (second measurement, recalculated) at 1073 K.
The enthalpy of mixing of Co with a liquid Sn-4.1Ag-1.3Cu (SAC387) alloy was determined by drop calorimetry up to a temperature difference of about 14 at. % at 1173 K and 1073 K, 4 at. % at 873 K and 3 at. % at 673 K. A clear difference was observed in the immediately measured heat effect, depending on the type of Co which was added: when a Co nanopowder was used, the observed heat effect was by about $7.5 \times 10^2$ J·mol$^{-1}$ more negative than for the use of bulk Co. It is shown that this difference has nothing to do with the molar enthalpy of mixing of liquid components but is caused by the excess surface enthalpy of the Co nanoparticles, eliminated during the dissolution process. This quantity is not dependent on the calorimeter temperature; it is determined only by the drop temperature, as all surface heat introduced into the calorimeter at drop temperature disappears during the dissolution of the nanoparticles into the liquid alloy, due to full elimination of their initial surface area.

**ACKNOWLEDGMENTS**

Financial support for this study came from the Austrian Science Fund (FWF) under project nos. P 26304 and P 27049. The authors also want to acknowledge the help of Prof. M. Zehetbauer and Prof. E. Schafer from the Faculty of Physics, University of Vienna, with the Sn-4.1Ag-1.3Cu foil preparation and Dr. St. Puchegger of the Faculty of Physics, University of Vienna, with the SEM studies. The work by G.K. was performed in the Centre of Applied Materials Science and Engineering at the University of Miskolc and within the framework of the TA MOP-4.2.2.A-11/1/KONV-2012-0019 project, and is carried out as part of the TA MOP-4.2.2.D-15/1/KONV-2015-0017 project in the framework of the New Széchenyi Plan, supported by the European Union, and cofinanced by the European Social Fund.

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DOI: 10.1021/acs.jpcch.5b09445
J. Phys. Chem. C 2016, 120, 1881–1890