The nano heat effect of replacing macro-particles by nano-particles in drop calorimetry: the case of core/shell metal/oxide nano-particles

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Experimental results are presented here obtained by a drop calorimetric method, in which Ni and Cu particles, both in bulk and nanosized form, were dropped into a liquid Sn-3.8Ag-0.7Cu solder alloy (in wt%). The molar enthalpies of mixing of the liquid (Sn-3.8Ag-0.7Cu)–Ni(Cu) alloys were measured. An extra exothermic heat effect is observed when dropping nano-particles instead of macro-particles. This is partly due to the loss of the large surface area and the corresponding large surface enthalpy of the nano-particles before their dissolution in the liquid alloy. However, a large additional exothermic heat effect was also found in the case of Cu-nano-particles, due to the exchange chemical reaction between the Cu₂O shell of the nano-particles and liquid Sn; this is caused by the fact that the Cu-nano-particles are core–shell particles with an inner metallic Cu core and an outer Cu₂O shell. This effect is less significant for Ni-nano-particles which have a thinner oxide shell.

Introduction

Nanostructured alloys represent a relatively novel class of materials compared to the conventional bulk ones, with a number of unique and promising features that have attracted an increasing number of scientists and engineers. However, there are still many open issues related to this research topic, such as the thermodynamic stability of the nanosized structures or the changes in properties during transition of the materials from the nanosized to bulk form.

At present, it is possible to produce nanoparticles (NPs) controlling not only their size but also their shape (spheres, plates, rods, etc.) and internal structure (metallic, bimetallic and multicomponent metal NPs), while the main progress in studies of the characteristics of NPs is achieved only in terms of size dependent thermodynamic properties. For instance, the shape-dependent changes of the melting temperature, cohesive energy, melting enthalpy and entropy were theoretically predicted and experimentally described in the literature. At the same time, there are only few studies dealing with changes in various other properties of NPs caused by their shape or internal structure. For instance, there is a number of papers dealing with the investigation of optical properties of metallic and bimetallic NPs. The extinction spectra of metal nanoparticles, such as Ag nanodisks and triangular prisms, Au multirods, as well as Au shell NPs with a pinhole (several nm) structure were investigated in ref. A bond-energy model for the calculation of the cohesive energy was developed in order to predict the size and shape dependency of various physical properties of metallic and bimetallic NPs with core/shell structure.

The explosive growth in the number of studies of some classes of materials is mostly related to their prospective application. For instance, in order to promote new enhanced and customer-friendly lead-free solders, nanocomposite Sn-based alloys with minor additions of metal nanoparticles have been under intensive scientific examination. Unfortunately, most of these studies refer to mechanical properties while information related to thermophysical and thermodynamic properties as well as structural features, especially in the liquid state, is scarce. However, a possible industrial use requires comprehensive data on new nanosized materials with precisely controlled properties. In particular, one needs reliable information on the thermodynamic stability of the employed metal nanoparticles in the bulk solder with respect to their possible dissolution during long time use. Therefore, new studies dealing with chemical and physical properties of metal NPs in a bulk metal matrix, depending on size, shape, composition, and structure of these NPs, are demanded.
Table 1  Enthalpies of mixing data for the addition of bulk Cu into the liquid Sn-4.2Ag alloy; standard states: pure liquid metals

| Mol. Cu dropped \( n_{\text{Cu}} (10^{-3}) \text{ mol} \) | Measured enthalpy \( \Delta H^o_{\text{signal}} (\text{J mol}^{-1}) \) | Partial molar enthalpy \( x_{\text{Cu}}^a \Delta M_{\text{Mol}} H_{\text{Cu}} (\text{J mol}^{-1}) \) | Integral molar enthalpy \( x_{\text{Cu}}^b \Delta M_{\text{Mol}} H (\text{J mol}^{-1}) \) |
|---|---|---|---|
| 0.5684 | 33 518 ± 604 | 0.0064 | −506 ± 958 | 0.0129 | 91 ± 7 |
| 0.4250 | 33 165 ± 513 | 0.0176 | −858 ± 1049 | 0.0223 | 82 ± 11 |
| 0.4547 | 33 350 ± 552 | 0.0272 | −673 ± 1054 | 0.0321 | 73 ± 24 |
| 0.5055 | 33 081 ± 609 | 0.0375 | −942 ± 1046 | 0.0428 | 62 ± 37 |
| 0.5484 | 33 167 ± 622 | 0.0485 | −856 ± 1049 | 0.0542 | 51 ± 50 |
| 0.5490 | 32 832 ± 656 | 0.0598 | −1191 ± 1038 | 0.0653 | 36 ± 64 |
| 0.5543 | 32 678 ± 659 | 0.0708 | −1345 ± 1033 | 0.0763 | 20 ± 77 |
| 0.5728 | 32 278 ± 673 | 0.0818 | −1737 ± 1021 | 0.0874 | −1290 |
| 0.5735 | 32 305 ± 674 | 0.0928 | −1718 ± 1021 | 0.0982 | −21 ± 103 |
| 0.5861 | 32 147 ± 686 | 0.1036 | −1876 ± 1016 | 0.1090 | −43 ± 115 |
| 0.6221 | 31 584 ± 715 | 0.1146 | −2439 ± 999 | 0.1201 | −73 ± 128 |
| 0.6412 | 31 509 ± 735 | 0.1258 | −2514 ± 996 | 0.1314 | −104 ± 141 |
| 0.6621 | 31 693 ± 764 | 0.1370 | −2330 ± 1002 | 0.1427 | −133 ± 154 |
| 0.6729 | 31 618 ± 774 | 0.1483 | −2405 ± 1000 | 0.1538 | −163 ± 167 |
| 0.6892 | 31 383 ± 795 | 0.1595 | −2340 ± 992 | 0.1651 | −193 ± 180 |
| 0.6986 | 30 800 ± 783 | 0.1707 | −3223 ± 974 | 0.1762 | −236 ± 192 |
| 0.7058 | 30 738 ± 790 | 0.1816 | −3285 ± 972 | 0.1870 | −276 ± 204 |
| 0.8912 | 30 456 ± 988 | 0.1936 | −3567 ± 963 | 0.2003 | −330 ± 218 |
| 0.9026 | 30 035 ± 987 | 0.2068 | −3989 ± 950 | 0.2133 | −389 ± 232 |

\[ T = 1073 \text{ K}; \text{ starting amount: } n_{\text{Ag}} = 1.8224 \times 10^{-3} \text{ mol}; n_{\text{Sn}} = 41.8071 \times 10^{-3} \text{ mol} \]

\[ T = 873 \text{ K}; \text{ first measurement; starting amount: } n_{\text{Ag}} = 1.7980 \times 10^{-3} \text{ mol}; n_{\text{Sn}} = 41.2485 \times 10^{-3} \text{ mol} \]

\[ T = 873 \text{ K}; \text{ second measurement; starting amount: } n_{\text{Ag}} = 1.7652 \times 10^{-3} \text{ mol}; n_{\text{Sn}} = 40.4961 \times 10^{-3} \text{ mol} \]

* Average of \( x_{\text{Cu}} \) before and after drop. * Per mole of the mixture.
In the present study, a drop calorimetric method is used to investigate the “thermodynamic nanoeffects”. A Sn-3.8Ag-0.7Cu alloy (SAC387; in wt%) was employed in the performed study as the main component since SAC387 is a commercially available solder. Many papers are dealing with nanocomposite Sn–Ag–Cu (SAC) solders, attempting to improve their properties by minor additions of metal NPs such as Co, Cu, Fe, Ni, etc. The nanocomposite SAC solder is refloowed during the soldering process, and reactive metal NPs are dissolved in the liquid Sn-based matrix. Therefore, the present research provides essential data to simulate the soldering process using nanocomposite solders with nano-sized metal additions in a proper way. The heat effects caused by the dissolution of Cu and Ni in bulk as well as in nanosized form were determined and the excess surface enthalpies of the employed NPs were derived. The experimental results are theoretically described taking into account not only the size but also the internal structure of the nanoparticles, i.e. their apparent core–shell (metal core/oxide shell) structure.

Results and discussion

Calorimetric measurements. The present study was started with calorimetric measurements, adding pieces of bulk Cu into a liquid Sn-4.2Ag alloy (in at%) (Table 1), where the molar enthalpy of mixing for the liquid Sn-4.2Ag alloy was taken from Kister et al.17 Since the concentration values in figures and tables are given in at%, the composition of the SAC387 master alloy is also converted to at%, resulting in a composition Sn-4.1Ag-1.3Cu. The measurements were performed at 1073 K and 873 K; they were compared with data calculated by a Redlich–Kister–Muggianu polynomial by adding an additional term corresponding to symmetric quaternary interactions.24 As seen from Fig. 2, there is a reasonably good agreement between experimental and calculated data with a maximum difference of less than 1 kJ mol⁻¹.

The results in Table 3 differ from those in Tables 1 and 2 by the experimental procedure: they were obtained by dropping pieces of Cu or Ni wrapped in a Sn-4.1Ag-1.3Cu foil into the liquid alloy in the calorimeter at 1073 K and 873 K. These measurements were performed to ensure that no significant side effects would be observed when dropping NPs wrapped into such a foil into the calorimeter. As seen from Fig. 3a and b, very good agreement was obtained between experimental results with and without employing the Sn-4.1Ag-1.3Cu foil. It should also be noted that, in contrast to the ternary Ag–Cu–Sn alloys (Fig. 1), the quaternary Ag–Cu–Ni–Sn alloys did not show any significant temperature dependence of the molar mixing enthalpies (Fig. 2 and 3b). The present results of the partial enthalpy of mixing for ternary and quaternary alloys were exothermic in the investigated concentration range at both temperatures while the integral enthalpy of mixing for the ternary (Sn-4.1Ag-1.3Cu)–Cu alloys changes from positive to negative values with increasing Cu content. Furthermore, the experimental data for the ternary (Sn-4.1Ag-1.3Cu)–Cu alloys indicated a clear temperature and concentration dependence of the integral enthalpy of mixing, with a tendency to more exothermic values at lower temperatures and higher Cu contents.

The microstructure analysis of the samples after calorimetric measurements showed that the intermetallic compounds (IMCs) Ag₃Sn, Cu₆Sn₅ and Ni₃Sn₄ had been formed during the solidification of the investigated Ag–Cu–Ni–Sn samples (Fig. 4a–d, Table 4). These results are in very good agreement with the quaternary Ag–Cu–Ni–Sn phase diagram.27 According to SEM analyses of the investigated samples, a substitution of Ni and Cu atoms, respectively, was observed in the IMCs Cu₆Sn₅ and Ni₃Sn₄. This effect is more pronounced for (Cu,Ni)₆Sn₅ due to a significantly increasing exothermic enthalpy of formation of this compound on admixture of Ni.28 In the Sn₇₅Ag₅Cu₂₅ alloy, two Cu–Sn IMCs were found, namely Cu₃Sn and Cu₄Sn₃. According to the Cu–Sn phase diagram, Cu₄Sn₃ should be formed in the investigated alloy during cooling and should decompose under equilibrium conditions into pure Sn and Cu₄Sn₃ at 681 K.29 However, the cooling of the sample after the calorimetric measurement was certainly not slow enough to reach an equilibrium state, thus Cu₄Sn₃ grains are left as can be seen in the microstructure.

After the experiments with bulk Cu and Ni, the corresponding experiments with nano-particles were performed (Tables 5 and 6). The excess enthalpies due to the nano-effect were...
Table 2 Enthalpies of mixing data for the addition of bulk Ni into the liquid Sn-4.1Ag-1.3Cu alloy; standard states: pure liquid metals

| Mol. Ni dropped (10⁻³ mol) | Measured enthalpy | Partial molar enthalpy | Integral molar enthalpy |
|---------------------------|-------------------|------------------------|-------------------------|
| nNi                      | ΔH_{mix}^{ex} (J mol⁻¹) | xNi   | ΔMiH_{Ni} (J mol⁻¹) | xNi | ΔMiH (J mol⁻¹) |
| 1.1040                   | -9226 ± 667       | 0.0132 | -49894 ± 650       | 0.0263 | -1225 ± 16 |
| 1.1889                   | -9214 ± 718       | 0.0398 | -49882 ± 649       | 0.0532 | -2567 ± 32 |
| 1.2866                   | -10252 ± 864      | 0.0669 | -50920 ± 723       | 0.0806 | -3969 ± 51 |
| 1.3084                   | -10061 ± 863      | 0.0938 | -50729 ± 709       | 0.1069 | -5307 ± 68 |
| 1.6360                   | -11267 ± 1208     | 0.1224 | -51935 ± 794       | 0.1378 | -6919 ± 91 |

T = 1073 K; starting amount: nAg = 1.6901 × 10⁻³ mol; nCu = 0.5285 × 10⁻³ mol; nSn = 38.5956 × 10⁻³ mol

| Mol. Ni dropped (10⁻³ mol) | Measured enthalpy | Partial molar enthalpy | Integral molar enthalpy |
|---------------------------|-------------------|------------------------|-------------------------|
| nNi                      | ΔH_{mix}^{ex} (J mol⁻¹) | xNi   | ΔMiH_{Ni} (J mol⁻¹) | xNi | ΔMiH (J mol⁻¹) |
| 0.2259                   | -9155 ± 135       | 0.0026 | -49719 ± 643       | 0.0052 | -169 ± 15 |
| 0.2769                   | -9283 ± 168       | 0.0084 | -49848 ± 652       | 0.0115 | -485 ± 30 |
| 0.3012                   | -9718 ± 191       | 0.0149 | -50282 ± 683       | 0.0183 | -827 ± 45 |
| 0.3641                   | -9669 ± 230       | 0.0224 | -50234 ± 680       | 0.0264 | -1234 ± 60 |
| 0.3723                   | -9784 ± 238       | 0.0305 | -50349 ± 688       | 0.0345 | -1644 ± 75 |
| 0.3743                   | -9825 ± 240       | 0.0386 | -50390 ± 691       | 0.0426 | -2050 ± 90 |
| 0.4248                   | -10111 ± 280      | 0.0471 | -50576 ± 711       | 0.0515 | -2505 ± 105 |
| 0.4646                   | -10129 ± 307      | 0.0564 | -50691 ± 712       | 0.0612 | -2993 ± 119 |
| 0.5238                   | -9884 ± 338       | 0.0665 | -50449 ± 695       | 0.0718 | -3529 ± 133 |
| 0.5556                   | -10511 ± 381      | 0.0773 | -51076 ± 739       | 0.0828 | -4092 ± 147 |
| 0.5738                   | -11319 ± 424      | 0.0883 | -51884 ± 796       | 0.0938 | -4669 ± 162 |
| 0.5936                   | -11034 ± 428      | 0.0994 | -51599 ± 775       | 0.1050 | -5249 ± 176 |
| 0.6200                   | -11567 ± 468      | 0.1107 | -52132 ± 813       | 0.1164 | -5845 ± 190 |
| 0.6274                   | -11251 ± 461      | 0.1220 | -51816 ± 791       | 0.1276 | -6430 ± 204 |
| 0.6874                   | -12276 ± 551      | 0.1336 | -52841 ± 863       | 0.1396 | -7067 ± 218 |

T = 1073 K; second measurement; starting amount: nAg = 1.7825 × 10⁻³ mol; nCu = 0.5574 × 10⁻³ mol; nSn = 40.7056 × 10⁻³ mol

| Mol. Ni dropped (10⁻³ mol) | Measured enthalpy | Partial molar enthalpy | Integral molar enthalpy |
|---------------------------|-------------------|------------------------|-------------------------|
| nNi                      | ΔH_{mix}^{ex} (J mol⁻¹) | xNi   | ΔMiH_{Ni} (J mol⁻¹) | xNi | ΔMiH (J mol⁻¹) |
| 0.3080                   | -18322 ± 397      | 0.0037 | -52664 ± 1108      | 0.0074 | -242 ± 10 |
| 0.3278                   | -18316 ± 423      | 0.0113 | -52638 ± 1108      | 0.0152 | -625 ± 20 |
| 0.5430                   | -17950 ± 686      | 0.0215 | -52292 ± 1086      | 0.0278 | -1312 ± 35 |
| 0.5684                   | -18800 ± 752      | 0.0342 | -53142 ± 1137      | 0.0406 | -1997 ± 53 |

T = 873 K; first measurement; starting amount: nAg = 1.7086 × 10⁻³ mol; nCu = 0.5343 × 10⁻³ mol; nSn = 39.0184 × 10⁻³ mol

| Mol. Ni dropped (10⁻³ mol) | Measured enthalpy | Partial molar enthalpy | Integral molar enthalpy |
|---------------------------|-------------------|------------------------|-------------------------|
| nNi                      | ΔH_{mix}^{ex} (J mol⁻¹) | xNi   | ΔMiH_{Ni} (J mol⁻¹) | xNi | ΔMiH (J mol⁻¹) |
| 1.2447                   | -18830 ± 1419     | 0.0072 | -53125 ± 1140      | 0.0144 | -619 ± 16 |
| 1.2190                   | -18733 ± 1383     | 0.0213 | -53029 ± 1135      | 0.0281 | -1349 ± 32 |
| 0.4438                   | -18926 ± 509      | 0.0306 | -53221 ± 1146      | 0.0331 | -1610 ± 38 |
| 0.4800                   | -18996 ± 552      | 0.0357 | -53291 ± 1150      | 0.0383 | -1891 ± 44 |
| 0.4846                   | -18669 ± 548      | 0.0409 | -52965 ± 1131      | 0.0435 | -2169 ± 50 |
| 0.5128                   | -18822 ± 585      | 0.0463 | -53117 ± 1140      | 0.0490 | -2461 ± 56 |
| 0.5463                   | -19068 ± 631      | 0.0519 | -53364 ± 1155      | 0.0548 | -2770 ± 63 |

\(a\) Average of \(x_{Ni}\) before and after drop. \(b\) Per mole of the mixture.

estimated, similarly as in ref. 19, by comparing the measured enthalpy values obtained with bulk and nanosized particles (Fig. 5 and 6).

In order to estimate values of the excess enthalpy, the concentration dependencies of the measured enthalpy for additions of Cu and Ni in bulk and nanosized form were plotted as a function of the content of the added element and extrapolated to zero. The estimated value of \(\Delta H_{mix}^{ex}\) for Cu additions was found to be about \(-17.0 \pm 1.2\) kJ mol⁻¹ at 1073 K and \(-18.5 \pm 1.3\) kJ mol⁻¹ at 873 K (Fig. 5). The corresponding value of \(\Delta H_{mix}^{ex}\) for Ni was found as about \(-3.8 \pm 1.6\) kJ mol⁻¹ at 1073 K and \(-3.3 \pm 1.5\) kJ mol⁻¹ at 873 K (Fig. 6).

The TEM analysis together with HAADF STEM (high angle annular dark field – scanning transmission electron

![Image 2](integral enthalpy of mixing of liquid Sn-4.1Ag-1.3Cu alloys)
Table 3: Enthalpies of mixing data for the addition of both packed bulk Cu and Ni into the liquid Sn-4.1Ag-1.3Cu alloy; standard states: pure liquid metals

| Mol. packed dropped metal | Measured enthalpy | Partial molar enthalpy | Integral molar enthalpy |
|---------------------------|-------------------|------------------------|------------------------|
| $n_{Cu}$ (10⁻³ mol)       | $\Delta H_{\text{signal}}$ (J mol⁻¹) | $x_{Cu}a$ | $\Delta_{\text{mix}}H_{Cu}$ (J mol⁻¹) | $x_{Cu}b$ | $\Delta_{\text{mix}}H$ (J mol⁻¹) |
| 0.6101                    | 33 431 ± 654      | 0.0060                | -427 ± 1072            | 0.0121    | 85 ± 13                     |
| 0.6273                    | 33 021 ± 692      | 0.0181                | -837 ± 1103            | 0.0241    | 73 ± 26                     |
| 0.6580                    | 32 527 ± 722      | 0.0302                | -1331 ± 1098           | 0.0363    | 56 ± 40                     |
| 0.6816                    | 32 532 ± 761      | 0.0425                | -1326 ± 1117           | 0.0486    | 38 ± 53                     |
| 0.7116                    | 32 707 ± 790      | 0.0548                | -1151 ± 1110           | 0.0610    | 22 ± 67                     |
| 0.7181                    | 32 267 ± 821      | 0.0670                | -1592 ± 1144           | 0.0731    | 1 ± 8                      |
| 0.7284                    | 32 090 ± 789      | 0.0790                | -1768 ± 1083           | 0.0849    | -22 ± 94                    |
| 0.7326                    | 32 363 ± 787      | 0.0907                | -1495 ± 1075           | 0.0965    | -42 ± 106                   |
| 0.7487                    | 31 614 ± 862      | 0.1022                | -2244 ± 1152           | 0.1079    | -69 ± 119                   |
| 0.7657                    | 31 775 ± 857      | 0.1135                | -2083 ± 1119           | 0.1191    | -96 ± 132                   |
| 0.7762                    | 31 465 ± 813      | 0.1247                | -2393 ± 1048           | 0.1302    | -125 ± 144                  |
| 0.7933                    | 31 575 ± 877      | 0.1357                | -2284 ± 1105           | 0.1411    | -153 ± 156                  |
| 0.8448                    | 31 104 ± 859      | 0.1468                | -2754 ± 1017           | 0.1525    | -188 ± 167                  |
| 0.8656                    | 31 181 ± 893      | 0.1582                | -2677 ± 1031           | 0.1638    | -222 ± 178                  |
| 0.8783                    | 30 703 ± 853      | 0.1694                | -3155 ± 971            | 0.1750    | -262 ± 189                  |
| 0.9206                    | 30 828 ± 906      | 0.1807                | -3030 ± 984            | 0.1864    | -301 ± 200                  |
| 0.9556                    | 30 679 ± 965      | 0.1920                | -3179 ± 1010           | 0.1976    | -342 ± 211                  |
| 0.9794                    | 30 405 ± 1046     | 0.2031                | -3453 ± 1068           | 0.2086    | -385 ± 223                  |
| 1.1165                    | 29 964 ± 972      | 0.2149                | -3894 ± 871            | 0.2213    | -443 ± 233                  |
| 1.1578                    | 29 959 ± 960      | 0.2278                | -3900 ± 830            | 0.2343    | -501 ± 243                  |

$^a$ Average of $x_{Cu}/x_{Ni}$ before and after drop. $^b$ Per mole of the mixture.

$T = 1073$ K; starting amount: $n_{Ag} = 2.0639 \times 10^{-3}$ mol; $n_{Cu} = 0.6454 \times 10^{-3}$ mol; $n_{Sn} = 47.1327 \times 10^{-3}$ mol

$T = 1073$ K; starting amount: $n_{Ag} = 3.6576 \times 10^{-3}$ mol; $n_{Cu} = 1.1436 \times 10^{-3}$ mol; $n_{Sn} = 83.5197 \times 10^{-3}$ mol

$T = 873$ K; starting amount: $n_{Ag} = 3.5799 \times 10^{-3}$ mol; $n_{Cu} = 1.194 \times 10^{-3}$ mol; $n_{Sn} = 81.7527 \times 10^{-3}$ mol

Furthermore, EDX elemental mapping of Cu NPs showed an oxide shell (Cu₂O) covering a metal core (Fig. 7(a–c)). These data are in a good agreement with XRD analysis indicating the presence of both Cu and Cu₂O (cubic, see ref. 30) in the investigated Cu nanopowder (Fig. 9a). In the case of Ni NPs, only traces of NiO (trigonal/rhombohedral, see ref. 31) with very low intensity were found in the XRD pattern (Fig. 9b); only minor

microscopy) imaging should bring essential information about the characteristics of the employed Cu and Ni NPs in order to explain the significant difference in the values of the excess surface enthalpy. Fig. 7 and 8 show examples of the TEM micrographs of Cu and Ni NPs which show that the NPs (including oxide shell) are of similar size, considering the original size distribution.
amounts of oxygen were found on the surface of the Ni NPs (Fig. 8b and c). The first broad peak in the X-ray patterns is caused by the specimen holder with the polycarbonate cap.

Pore size distributions of Cu and Ni NPs were measured by nitrogen sorption according to the theory of Barrett, Joyner and Halenda (BJH) (Fig. 10a and b). The determined BET surface area of the employed NPs is equal to (10.6 ± 0.4) $10^3$ m$^2$ kg$^{-1}$ for Cu NPs and (10.2 ± 0.4) $10^3$ m$^2$ kg$^{-1}$ for Ni NPs.

Fig. 3 Integral enthalpy of mixing of liquid (Sn-4.1Ag-1.3Cu)$_{100-y}$Cu$_y$ alloys at 1073 K (a) and (Sn-4.1Ag-1.3Cu)$_{100-y}$Ni$_y$ alloys at 1073 K and 873 K (b).

Fig. 4 BSE micrographs of (Sn-4.1Ag-1.3Cu)$_{100-y}$Cu$_y$ (a) = Sn$_{76}$Ag$_3$Cu$_{11}$; (b) = Sn$_{83}$Ag$_4$Cu$_1$; (Sn-4.1Ag-1.3Cu)$_{100-y}$Ni$_y$ (c) = Sn$_{81}$Ag$_4$Cu$_1$Ni$_4$; (d) = Sn$_{82}$Ag$_4$Cu$_1$Ni$_4$) samples after calorimetry.

Theoretical considerations

The goal of this chapter is to model the observed $\Delta H^\text{ex}_{\text{nano}}$ values by applying the principles of nano-thermodynamics.\textsuperscript{19-34} In a previous paper\textsuperscript{29} the nano-effect was described as

$$\Delta H^\text{ex}_{\text{nano}} = -A_{\text{BET}}M_s^0 \sigma_{s\gamma,H,T_0},$$  

(1)

where $A_{\text{BET}}$ (m$^2$ g$^{-1}$) is the BET surface area of the nano-particles (which is assumed to be negligible for bulk material), $M$ (g mol$^{-1}$) is the molar mass of the nano-particles, $\sigma_{s\gamma,H,T_0}$ (J m$^{-2}$) is the enthalpy part of the surface energy of the solid nano-particles at the drop temperature. (Note that in the present paper the sign of $\Delta H^\text{ex}_{\text{nano}}$ is kept positive contrary to the previous paper,\textsuperscript{39} thus a negative sign appears in eqn (1); this is done for two reasons: to avoid predicting anything before the experiments are run, and to make more obvious that the nano-effect is exothermic). The physical meaning of eqn (1) is the loss (see the negative sign) of the enthalpy part of the surface energy of the nano-particles upon dissolution per mole of metal added. The calculated and experimental results for the systems studied in this paper are compared in Table 7.

As follows from Table 7, the experimental values in this case are considerably more negative than the calculated ones, and this difference is especially striking for Cu nanoparticles. This is most probably due to the fact that eqn (1) is strictly valid only for pure metallic nano-particles without any oxide shell. However, as observed by the TEM and XRD investigations of the nano-particles (see Fig. 6–8), the Cu-nano-particles are severely contaminated by oxygen. Actually, instead of Cu-nano-particles we have core/shell nano-particles with a Cu inner core ($\alpha$) and a Cu$_2$O shell ($\beta$), which form together particle $\gamma$. A similar oxidation problem exists also for Ni nano-particles, however, to a much smaller extent. Therefore, the previous model in eqn (1) has to be modified to take into account the role of the oxide shells on the metallic nano-particles, too.

When the experiments were performed, it was assumed that $n^0_{\text{Me}}$ (mole) of pure metal was added into the calorimeter. Instead, the molar part $\gamma$ of these nano-particles was actually oxidized so that in fact the following amounts of matter were added:

$$n_\alpha = (1 - \gamma)n^0_{\text{Me}},$$  

(2)

$$n_\beta = \gamma n^0_{\text{Me}},$$  

(3)

where $\alpha$ denotes the added metal, and $\beta$ denotes its oxide shell MeO$_x$ (where the stoichiometry is always written such that the oxide molecule contains one metallic atom, i.e., $x$ can be any positive number). Thus, in addition to eqn (1), there are two additional terms for the enthalpy nano-effect: one is responsible for different heat capacities of $\alpha$ (metal) and $\beta$ (oxide), while the other one is responsible for the chemical interaction between $\beta$ and metal atoms in the liquid alloy (in our case these are mostly atoms of Sn), into which the nano-particles are added:

$$\Delta H^\text{ex}_{\alpha/\beta,\text{nano}} = -A_{\text{BET}}M_s^0 \sigma_{s\gamma,H,T_0} + \gamma(\Delta H^\gamma_C + \Delta H^\gamma_0),$$  

(4)
where $M_f$ is the average molar mass of the partly oxidized particle as defined by eqn (5), $\sigma_{s,T_0}$ is the effective enthalpy part of the surface energy of the partly oxidized particle as defined by eqn (6), and $\Delta H_c$ (J mol$^{-1}$) is the enthalpy difference due to the different heat capacities of the oxide and the metal as defined by eqn (7); $\Delta H_f$ (J mol$^{-1}$) is the standard molar enthalpy change of the chemical reaction: $\text{MeO} + y\text{Sn} = \text{Sn}_x\text{O}_y + \text{Me}$ (or, which is the same: $\beta + y\text{Sn} = \text{Sn}_x\text{O}_y + \alpha$, where the stoichiometry is always written such that the oxide molecule contains one metallic atom, i.e., $x$ can be any positive number):

$$M_f = (1 - y)M_a + yM_\beta,$$

$$\sigma_{s,T_0} \equiv \sigma_{s,0} + \beta_0 H_{s,0} + (\sigma_{s,0} - \sigma_{s,0}) \exp \left(-\frac{d}{\beta_0}\right),$$

$$\Delta H_c = \int_{T_0}^{T_M} (C_p, \beta - C_p, a) dT,$$

where $M_a$ (g mol$^{-1}$) is the molar mass of the metal core, $M_\beta$ (g mol$^{-1}$) is the molar mass of the oxide shell, $\sigma_{s,0}$ (J m$^{-2}$) is the enthalpy part of the $\alpha/\beta$ interfacial energy, $\sigma_{s,0}$ (J m$^{-2}$) is the enthalpy part of the surface energy of the oxide shell, $\sigma_{s,0}$ (J m$^{-2}$) is the enthalpy part of the surface energy of the metallic core, $d$ (nm) is the thickness of the oxide shell, $\beta$ $\equiv$ 1 nm is the coefficient in the separation dependence of interfacial energies, $a$ $C_p, \beta$ (J mol$^{-1}$) is the molar heat capacity of the oxide shell of the nano-particle, $C_p, a$ (J mol$^{-1}$) is the molar heat capacity of the metallic inner core of the nano-particle. When the oxide shell is thin, it is modelled as a shell of constant thickness following the original shape of the nano-particle. If this thickness is much smaller than the radius of the nano-particle, the BET surface area of the outer oxide/gas surface and the BET interfacial area of the inner metal/oxide interface are considered equal.

In order to check whether the proposed reactions are exergonic and favorable or not, the free energy change for the reactions was estimated from the Gibbs energy of formation values of the oxides of copper ($\Delta G_{\text{CuO}}$), nickel ($\Delta G_{\text{NiO}}$) and tin ($\Delta G_{\text{SnO}}$). In the present case, there are two chemical exchange reactions, i.e. ($\text{Cu}_2\text{O} + 2\text{Sn} = 2\text{Sn}_2\text{O}_2 + 2\text{Cu}$) and ($\text{NiO} + 2\text{Sn} = 2\text{Sn}_2\text{O}_3 + \text{Ni}$). It is assumed that the Gibbs energy change for the first reaction can be obtained as $\Delta G_{\text{Sn}_2\text{O}_3} = 1/2(\Delta G_{\text{SnO}} - 2\Delta G_{\text{NiO}})$ and that for the second reaction as $\Delta G_{\text{Cu}_2\text{O}} = 1/2\Delta G_{\text{SnO}} - \Delta G_{\text{CuO}}$. The Gibbs energies of formation for the oxides at 1073 K and 873 K were taken from ref. 37 and 38. Based on the obtained results, the calculated Gibbs energy change for the reactions is exothermic at both temperatures and equals $-93.3$ kJ mol$^{-1}$ and $-86.9$ kJ mol$^{-1}$ for $\Delta G_{\text{Cu}_2\text{O}/\text{SnO}_2}$ and $-38.2$ kJ mol$^{-1}$ and $-34.5$ kJ mol$^{-1}$ for $\Delta G_{\text{NiO}/\text{SnO}_2}$ at 873 K and 1073 K, respectively.

The amount of matter of the oxide shell can be expressed from its geometry as:

$$n = A_B \beta \rho_B n_0 \bar{n},$$

where $\bar{n}$ (g m$^{-3}$) is the density of the oxide shell. The quantities expressed by eqn (3) and (8) are equal. Consequently, the thickness of the oxide shell ($d$) can be expressed as function of the mole fraction of the oxidized part of the nano-particle ($y$), as:

$$d = \frac{d}{\bar{n}}.$$

Let us also mention that for $y = 0$, eqn (4) becomes identical to eqn (1), being a reasonable boundary condition. Substituting eqn (5)-(7) and (9) into eqn (4), the excess nano heat effect can be calculated as function of $y$ for partly oxidized metallic nanoparticles.

The corresponding constants are given in Table 7. In this paper, the selection Sn was made (for the values in the last column of Table 8), as Sn has the highest affinity towards oxygen and the highest mole fraction in the liquid alloy among its components (Sn, Cu, Ag). The results calculated based on Table 8 are compared with experimental data in Fig. 11 and 12.

As follows from Fig. 11 and 12, the experimental results can be reproduced with $y = 0.24 \pm 0.02$ for Cu-nanoparticles and with $y = 0.039 \pm 0.004$ for Ni-nanoparticles. These values are in qualitative agreement with Fig. 7–9. Thus, our new extended model is able to describe the nano heat effect for the dissolution of partly oxidized nanoparticles.

### Experimental

The heat effects of small additions of Cu and Ni to the liquid SAC387 alloy were investigated by a drop calorimetric

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**Table 4** SEM-EDX results of $(\text{Sn-4.1Ag-1.3Cu})_{100-x}\text{Cu}_x$ and $(\text{Sn-4.1Ag-1.3Cu})_{100-x}\text{Ni}_x$ samples after calorimetry

| Sample | Temperature of calor. meas. (K) | Dropped component | Sn at% | Ag at% | Sn at% | Cu at% | Ni at% | Sn at% |
|--------|--------------------------------|------------------|--------|--------|-------|--------|--------|-------|
| $\text{Sn}_2\text{Ag}_3\text{Cu}_{14}$ | 1073 | bulk Cu | $\beta\text{Sn}$ | 100 | 25 | $\text{Cu}_4\text{Sn}_5$ | 53 | 47 |
| 1st meas. | | | | | | | | |
| $\text{Sn}_4\text{Ag}_3\text{Cu}_{13}$ | 873 | nano Cu | $\beta\text{Sn}$ | 100 | 27 | $\text{Cu}_4\text{Sn}_5$ | 53 | 47 |
| 2nd meas. | | | | | | | | |
| $\text{Sn}_4\text{Ag}_3\text{Ni}_{14}$ | 1073 | bulk Ni | $\beta\text{Sn}$ | 100 | 24 | $(\text{Cu},\text{Ni})\text{Sn}_5$ | 34 | 18 | 48 |
| 1st meas. | | | | | | | | |
| $\text{Sn}_4\text{Ag}_3\text{Ni}_{14}$ | 873 | nano Ni | $\beta\text{Sn}$ | 100 | 27 | $(\text{Cu},\text{Ni})\text{Sn}_5$ | 34 | 19 | 50 |
| 1st meas. | | | | | | | | |
Table 5  Enthalpies of mixing data for the addition of nano Cu into the liquid Sn-4.1Ag-1.3Cu alloy: standard states: pure liquid metals

| Mol nano-sized Cu dropped | Measured enthalpy | Partial molar enthalpy | Integral molar enthalpy |
|---------------------------|-------------------|------------------------|------------------------|
| $n_{Cu}$ (10^{-3} mol)    | $\Delta H_{mix}^\circ$ (J mol^{-1}) | $x_{Cu}^a$ | $\Delta M_H^{-1}H_{Cu}$ (J mol^{-1}) | $x_{Cu}^b$ | $\Delta M_H^{-1}H$ (J mol^{-1}) |
| $T = 1073$ K; first measurement; starting amount: $n_{Ag} = 1.9452 \times 10^{-3}$ mol; $n_{Cu} = 0.6083 \times 10^{-3}$ mol; $n_{Sn} = 44.4216 \times 10^{-3}$ mol | | | | |
| 0.2233 | 34.199 ± 637 | 0.0024 | 14 ± 1104 | 0.0047 | 91 ± 13 |
| 0.2161 | 33.758 ± 629 | 0.0069 | −427 ± 1127 | 0.0091 | 9 ± 26 |
| 0.2504 | 34.010 ± 633 | 0.0116 | −175 ± 979 | 0.0141 | −68 ± 39 |
| 0.2546 | 33.692 ± 627 | 0.0166 | −492 ± 954 | 0.0191 | −157 ± 51 |
| 0.2747 | 33.839 ± 630 | 0.0217 | −346 ± 888 | 0.0243 | −243 ± 63 |
| 0.2747 | 33.463 ± 623 | 0.0268 | −722 ± 878 | 0.0294 | −337 ± 74 |
| 0.3087 | 33.676 ± 627 | 0.0321 | −509 ± 787 | 0.0349 | −426 ± 85 |
| 0.3298 | 33.606 ± 622 | 0.0378 | −579 ± 735 | 0.0407 | −524 ± 96 |
| 0.3360 | 33.156 ± 617 | 0.0436 | −1029 ± 712 | 0.0464 | −629 ± 106 |
| 0.3482 | 33.233 ± 619 | 0.0493 | −952 ± 688 | 0.0522 | −733 ± 116 |
| 0.3544 | 33.470 ± 623 | 0.0551 | −715 ± 681 | 0.0580 | −836 ± 126 |
| 0.3562 | 33.910 ± 613 | 0.0690 | −1275 ± 666 | 0.0647 | −943 ± 136 |
| 0.3624 | 33.115 ± 617 | 0.0665 | −1069 ± 659 | 0.0692 | −1047 ± 145 |
| 0.3691 | 32.364 ± 603 | 0.0719 | −1821 ± 632 | 0.0746 | −1151 ± 153 |
| 0.3913 | 32.357 ± 619 | 0.0775 | −925 ± 613 | 0.0803 | −750 ± 161 |
| 0.5954 | 32.276 ± 601 | 0.0831 | −1909 ± 589 | 0.0860 | −1358 ± 169 |
| 0.4237 | 33.125 ± 617 | 0.0989 | −1059 ± 564 | 0.0918 | −1462 ± 177 |
| 0.4345 | 32.461 ± 604 | 0.0946 | −1724 ± 539 | 0.0974 | −1571 ± 184 |
| 0.6205 | 32.701 ± 609 | 0.1014 | −1483 ± 380 | 0.1054 | −1677 ± 190 |

$T = 1073$ K; second measurement; starting amount: $n_{Ag} = 1.9755 \times 10^{-3}$ mol; $n_{Cu} = 0.6177 \times 10^{-3}$ mol; $n_{Sn} = 45.1128 \times 10^{-3}$ mol

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| Mol nano-sized Cu dropped | Measured enthalpy | Partial molar enthalpy | Integral molar enthalpy |
|---------------------------|-------------------|------------------------|------------------------|
| $n_{Cu}$ (10^{-3} mol)    | $\Delta H_{mix}^\circ$ (J mol^{-1}) | $x_{Cu}^a$ | $\Delta M_H^{-1}H_{Cu}$ (J mol^{-1}) | $x_{Cu}^b$ | $\Delta M_H^{-1}H$ (J mol^{-1}) |
| $T = 873$ K; first measurement; starting amount: $n_{Ag} = 1.8702 \times 10^{-3}$ mol; $n_{Cu} = 0.5848 \times 10^{-3}$ mol; $n_{Sn} = 42.7094 \times 10^{-3}$ mol | | | | |
| 0.1134 | 26.783 ± 570 | 0.0012 | −1597 ± 1335 | 0.0025 | 144 ± 13 |
| 0.1199 | 26.873 ± 572 | 0.0038 | −1508 ± 1266 | 0.0051 | 93 ± 25 |
| 0.1321 | 26.885 ± 572 | 0.0065 | −1495 ± 1150 | 0.0079 | 39 ± 37 |
| 0.1296 | 26.849 ± 570 | 0.0092 | −1532 ± 1171 | 0.0106 | −20 ± 49 |
| 0.1338 | 27.048 ± 576 | 0.0120 | −1332 ± 1143 | 0.0134 | −75 ± 61 |
| 0.1379 | 26.691 ± 568 | 0.0147 | −1689 ± 1094 | 0.0161 | −133 ± 72 |
| 0.1462 | 26.922 ± 573 | 0.0176 | −1458 ± 1041 | 0.0190 | −190 ± 83 |
| 0.1501 | 26.819 ± 571 | 0.0205 | −1562 ± 1009 | 0.0220 | −251 ± 95 |
| 0.1519 | 26.460 ± 563 | 0.0235 | −1921 ± 984 | 0.0249 | −313 ± 105 |
| 0.1677 | 26.439 ± 563 | 0.0265 | −1942 ± 891 | 0.0281 | −375 ± 116 |
| 0.1779 | 26.667 ± 568 | 0.0298 | −1714 ± 834 | 0.0314 | −442 ± 126 |
| 0.1892 | 26.616 ± 566 | 0.0332 | −1765 ± 795 | 0.0349 | −511 ± 136 |
| 0.1914 | 26.425 ± 562 | 0.0366 | −1956 ± 780 | 0.0383 | −584 ± 146 |
| 0.1980 | 26.148 ± 557 | 0.0401 | −2233 ± 746 | 0.0418 | −658 ± 156 |
| 0.2129 | 25.925 ± 552 | 0.0437 | −2455 ± 688 | 0.0455 | −734 ± 164 |
| 0.2246 | 26.184 ± 557 | 0.0474 | −2197 ± 659 | 0.0494 | −813 ± 174 |
| 0.2343 | 26.097 ± 555 | 0.0513 | −2284 ± 630 | 0.0533 | −895 ± 182 |
Table 5  (Contd.)

| Mol nano-sized Cu dropped | Measured enthalpy | Partial molar enthalpy | Integral molar enthalpy |
|---------------------------|-------------------|------------------------|-------------------------|
| $n_{Cu}$ ($10^{-3}$ mol) | $\Delta H^*_\text{signal}$ (J mol$^{-1}$) | $x_{Cu}^a$ | $\Delta_{\text{Mol}}H_{Cu}$ (J mol$^{-1}$) | $x_{Cu}^b$ | $\Delta_{\text{Mol}}H$ (J mol$^{-1}$) |
| 0.3362 | 26 195 ± 558 | 0.0561 | −2186 ± 440 | 0.0589 | −981 ± 190 |
| 0.3904 | 25 837 ± 550 | 0.0621 | −2544 ± 374 | 0.0653 | −1104 ± 198 |
| 0.0850 | 25 601 ± 545 | 0.0658 | −2780 ± 1702 | 0.0664 | −1234 ± 206 |

$T = 873$ K; second measurement; starting amount: $n_M = 1.9152 \times 10^{-3}$ mol; $n_{Cu} = 0.5089 \times 10^{-3}$ mol; $n_{Sn} = 43.7365 \times 10^{-3}$ mol

$0.3188$ | 27 210 ± 571 | 0.0034 | −1143 ± 953 | 0.0068 | 140 ± 12 |
| 0.3780 | 26 649 ± 559 | 0.0107 | −1704 ± 787 | 0.0146 | −2−24 |
| 0.4311 | 26 564 ± 557 | 0.0185 | −1789 ± 736 | 0.0225 | −164 ± 35 |
| 0.4044 | 26 627 ± 559 | 0.0264 | −1725 ± 735 | 0.0303 | −329 ± 45 |
| 0.4038 | 26 629 ± 559 | 0.0340 | −1723 ± 736 | 0.0377 | −489 ± 55 |
| 0.4165 | 26 253 ± 551 | 0.0414 | −2100 ± 706 | 0.0452 | −646 ± 65 |
| 0.4239 | 26 231 ± 550 | 0.0488 | −2122 ± 691 | 0.0525 | −803 ± 75 |
| 0.4250 | 25 600 ± 537 | 0.0560 | −2753 ± 672 | 0.0595 | −961 ± 83 |
| 0.4375 | 25 995 ± 545 | 0.0630 | −2358 ± 663 | 0.0665 | −1113 ± 92 |
| 0.4487 | 25 936 ± 544 | 0.0700 | −2416 ± 645 | 0.0735 | −1263 ± 100 |
| 0.4675 | 25 889 ± 543 | 0.0770 | −2464 ± 618 | 0.0806 | −1413 ± 108 |
| 0.4745 | 25 845 ± 542 | 0.0840 | −2508 ± 608 | 0.0875 | −1565 ± 116 |
| 0.4820 | 25 517 ± 535 | 0.0909 | −2835 ± 591 | 0.0943 | −1717 ± 123 |
| 0.4834 | 25 315 ± 531 | 0.0976 | −3038 ± 584 | 0.1010 | −1867 ± 130 |
| 0.4838 | 25 371 ± 532 | 0.1042 | −2981 ± 585 | 0.1073 | −2015 ± 137 |
| 0.4957 | 25 077 ± 526 | 0.1104 | −3276 ± 565 | 0.1135 | −2317 ± 143 |
| 0.5133 | 25 438 ± 534 | 0.1167 | −2915 ± 553 | 0.1199 | −2295 ± 149 |
| 0.5271 | 24 826 ± 521 | 0.1231 | −3527 ± 526 | 0.1263 | −2440 ± 155 |
| 0.5745 | 25 129 ± 527 | 0.1297 | −3232 ± 488 | 0.1330 | −2583 ± 160 |

$^a$ Average of $x_{Cu}$ before and after drop. $^b$ Per mole of the mixture.

Method. The measurements were carried out using a Calvet-type twin microcalorimeter system under high purity Ar (99.9999%) flow (approximately 20−30 ml min$^{-1}$). The apparatus consists of two thermopiles containing more than 200 thermocouples, a commercial wire wound resistance furnace (HTC-1000, SETARAM, Lyon, France) and a self-made automatic drop device for up to 30 drops. The SAC387 alloy was placed in a BN crucible. The time interval between individual drops was 0.5 s. The calorimeter was calibrated by the drop series of each separate measurement. The microcalorimeter and the mechanical sampler were controlled through a self-provided software using the graphical programming environment LabVIEW. The obtained signals from the thermocouples were recorded and evaluated using the commercial HiQ® software. The microcalorimeter was described in detail elsewhere.43

In general, the measured enthalpy (integrated heat flow at constant pressure) for bulk materials is equal to:

$$\left(\Delta H^*_\text{Signal}\right)_\text{bulk} = n_i \left(\Delta H^*_\text{Signal}\right)_\text{bulk} = n_i \left(\Delta H^*_{\text{M.i.T}_W} - \Delta H^*_{\text{M.i.T}_D}\right) + \Delta H^*_{\text{Reaction}},$$

(10)

where $n_i$ is the number of moles of the added element $i$, $\Delta H^*_\text{Signal}$ is the measured enthalpy in J mol$^{-1}$, $H_M$ denotes molar enthalpies, $T_D$ is the drop temperature, and $T_M$ is the calorimeter temperature for the respective measurement in Kelvin. The molar enthalpy difference ($\Delta H^*_{\text{M.i.T}_M} - \Delta H^*_{\text{M.i.T}_D}$) was calculated using the SGTE data for pure elements.43

However, in the case of nanosized additions one must also take into account the additional heat effect caused by the excess (surface) enthalpy of the metal nanoparticles. Thus, eqn (10) for the addition in the nanosized form can be rewritten as$^{19}$:

$$\Delta H^*_{\text{Signal}} = n_i \left[\left(\Delta H^*_\text{Signal}\right)_\text{bulk} + \Delta H^*_{\text{ex}}\right] = n_i \left(\Delta H^*_{\text{M.i.T}_W} - \Delta H^*_{\text{M.i.T}_D}\right) + \Delta H^*_{\text{Reaction}} + n_i \Delta H^*_{\text{ex}},$$

(11)

where $\Delta H^*_{\text{ex}}$ is the excess enthalpy connected with the replacement of bulk material by nano-particles in J mol$^{-1}$. Therefore, in order to find the heat effect caused by the addition of material in nanosized form we must know the heat effect caused by the addition of the same material in bulk form.

Furthermore, due to the rather small masses of added component $i$, partial enthalpies can be calculated by:

$$\Delta_{\text{Mol}}H_i = \frac{\Delta H^*_{\text{Reaction}}}{n_i},$$

(12)

The integral molar enthalpy of mixing, $\Delta_{\text{Mol}}H$, was calculated by summing the respective reaction enthalpies and dividing by
## Table 6 Enthalpies of mixing data for the addition of nano Ni into the liquid Sn-4.1Ag-1.3Cu alloy; standard states: pure liquid metals

| \( n_{\text{Ni}} \) (10\(^{-3}\) mol) | Measured enthalpy \( \Delta H_{\text{fus}}^{\text{mix}} \) (J mol\(^{-1}\)) | Partial molar enthalpy \( x_{\text{Ni}} \) \( \Delta_{\text{mix}}H_{x_{\text{Ni}}} \) (J mol\(^{-1}\)) | Integral molar enthalpy \( x_{\text{Ni}} \) \( \Delta_{\text{mix}}H \) (J mol\(^{-1}\)) |
|-----------------|------------------------|-------------------------------|------------------------|
| 0.7417          | \(-13861 \pm 554\)     | 0.0041                        | \(-49400 \pm 543\)     | 0.0083                        | \(-318 \pm 5\)                 |
| 0.7656          | \(-13684 \pm 547\)     | 0.0124                        | \(-49222 \pm 516\)     | 0.0166                        | \(-759 \pm 9\)                 |
| 0.7858          | \(-13867 \pm 555\)     | 0.0207                        | \(-49406 \pm 512\)     | 0.0248                        | \(-1200 \pm 14\)               |
| 1.1022          | \(-13626 \pm 545\)     | 0.0305                        | \(-49164 \pm 357\)     | 0.0361                        | \(-1787 \pm 18\)               |
| 0.9387          | \(-13915 \pm 556\)     | 0.0409                        | \(-49453 \pm 422\)     | 0.0456                        | \(-2300 \pm 22\)               |
| 0.9615          | \(-13856 \pm 554\)     | 0.0502                        | \(-49394 \pm 418\)     | 0.0548                        | \(-2793 \pm 26\)               |
| 1.1326          | \(-14329 \pm 573\)     | 0.0601                        | \(-49867 \pm 372\)     | 0.0653                        | \(-3350 \pm 30\)               |
| 1.1366          | \(-14293 \pm 572\)     | 0.0704                        | \(-49382 \pm 369\)     | 0.0754                        | \(-3897 \pm 34\)               |
| 1.1458          | \(-13471 \pm 539\)     | 0.0804                        | \(-49010 \pm 338\)     | 0.0853                        | \(-4421 \pm 37\)               |
| 1.1778          | \(-14456 \pm 578\)     | 0.0902                        | \(-49994 \pm 362\)     | 0.0951                        | \(-4947 \pm 41\)               |
| 1.2029          | \(-14130 \pm 565\)     | 0.0999                        | \(-49669 \pm 343\)     | 0.1047                        | \(-5467 \pm 44\)               |
| 1.2095          | \(-14599 \pm 584\)     | 0.1095                        | \(-50137 \pm 357\)     | 0.1142                        | \(-5978 \pm 48\)               |
| 1.2590          | \(-14164 \pm 566\)     | 0.1189                        | \(-49720 \pm 329\)     | 0.1236                        | \(-6483 \pm 51\)               |
| 1.2684          | \(-15096 \pm 604\)     | 0.1281                        | \(-50635 \pm 356\)     | 0.1326                        | \(-6979 \pm 54\)               |
| 1.3939          | \(-14345 \pm 574\)     | 0.1375                        | \(-49884 \pm 303\)     | 0.1394                        | \(-7503 \pm 57\)               |
| 1.4623          | \(-15264 \pm 610\)     | 0.1474                        | \(-50803 \pm 314\)     | 0.1523                        | \(-8048 \pm 60\)               |
| 1.4931          | \(-15142 \pm 606\)     | 0.1572                        | \(-50681 \pm 304\)     | 0.1621                        | \(-8582 \pm 63\)               |
| 1.5044          | \(-14769 \pm 591\)     | 0.1668                        | \(-50308 \pm 292\)     | 0.1715                        | \(-9098 \pm 64\)               |

\( T = 1073 \text{ K; first measurement; starting amount: } n_{\text{Ag}} = 3.6656 \times 10^{-3} \text{ mol; } n_{\text{Cu}} = 1.1462 \times 10^{-3} \text{ mol; } n_{\text{Sn}} = 83.7083 \times 10^{-3} \text{ mol} \)

\[ \text{93} \]

\( T = 1073 \text{ K; second measurement; starting amount: } n_{\text{Ag}} = 1.7663 \times 10^{-3} \text{ mol; } n_{\text{Cu}} = 0.5523 \times 10^{-3} \text{ mol; } n_{\text{Sn}} = 40.3348 \times 10^{-3} \text{ mol} \)

\[ \text{93} \]

\( T = 873 \text{ K; first measurement; starting amount: } n_{\text{Ag}} = 1.9944 \times 10^{-3} \text{ mol; } n_{\text{Cu}} = 0.6236 \times 10^{-3} \text{ mol; } n_{\text{Sn}} = 45.5455 \times 10^{-3} \text{ mol} \)

\[ \text{152} \]

\( T = 873 \text{ K; second measurement; starting amount: } n_{\text{Ag}} = 1.8391 \times 10^{-3} \text{ mol; } n_{\text{Cu}} = 0.5751 \times 10^{-3} \text{ mol; } n_{\text{Sn}} = 41.9986 \times 10^{-3} \text{ mol} \)

\[ \text{152} \]

\( ^{a} \text{Average of } x_{\text{Ni}} \text{ before and after drop. } ^{b} \text{Per mole of the mixture.} \)
the total molar amount of substance, where \( n_j \) stands for the molar amount of substance which was already present in the crucible:

$$
\Delta_{\text{Mix}}H = \sum \Delta H_{\text{Reaction}}^{\text{Bulk}} n_j + \sum \Delta H_{\text{Reaction}}^{\text{Nano}} n_i.
$$

Prior to the measurements, the SAC387 alloy was prepared from Sn ingot (99.998% metallic purity), Ag shot (99.999% metallic purity) and Cu rods (99.9% metallic purity, all from Alfa Aesar, Karlsruhe, Germany) without further purification. The samples with a total mass between 5 and 10 g were sealed in evacuated quartz glass ampoules and kept in a muffle furnace for 2 weeks at 1173 K. The mass loss of the ingots was less than 0.1 mg.

The measurements were performed by dropping pure Ni or Cu, both in bulk and nanosized form. Ni pieces were obtained from Advent (99.99%; Oxford, UK), Ni and Cu nanopowders from IoLiTec Nanomaterials (Heilbronn, Germany). To avoid severe oxidation, all operations with nano-Ni and nano-Cu were
performed in a glovebox (M. Braun, LabMaster 130) under Ar atmosphere (Ar 5.0; O2 and H2O < 5 ppm each). The calorimetric measurements using the metal nanopowders were carried out similar to our previous thermodynamic investigations of nano-Co additions to liquid SAC387 alloys.19 the Ni and Cu nanoparticles were first packed into a SAC387 foil. The employed foil was produced from the same ingot using a foil rolling mill; it had a thickness of about 50 μm. The sample holders of the auto sampling device were loaded with nanopowder samples inside the glovebox and closed in a box, which was only taken out just before the measurement to be transported to the calorimeter. The calorimetric measurements with the packed nanoparticles were started with five drops of SAC387 foil pieces in order to determine and, subsequently, subtract the heat effect of the SAC387 foil from the obtained measured enthalpy. A few measurements with bulk Cu and Ni, packed into the SAC387 foil, were also carried out to prove the accuracy of this procedure.

Various factors must be considered when estimating the random and systematic errors in the measurements, i.e. the calorimeter construction, measuring method, calibration procedure, signal integration and “chemical errors”. Uncertainties of the enthalpy values given in Tables 1–6 were estimated based on the propagation of errors, taking also into account the standard deviation of the calorimeter constant s(k) which was evaluated by five drops of alumina for each run. The uncertainty of the partial enthalpy of mixing for each drop was calculated based on the uncertainties of peak areas of each drop, A0i of the amount of added component, ni, and s(k); the error of the integrated enthalpy of mixing was taken summing the errors of the single drops throughout the final composition. A similar procedure of calculation of the uncertainties of the enthalpy values was employed previously in ref. 44 and 45.

The phase composition and the microstructure of the samples were examined after the calorimetric measurements by powder X-ray diffraction (XRD; Bruker D8 Advance X-ray diffractometer) and scanning electron microscopy (SEM; Zeiss Supra 55 ESEM). The XRD analysis was carried out at ambient temperature using Ni-filtered Cu Kα radiation (accelerating voltage 40 kV, electron current 40 mA). The nanopowders were fixed onto the sample holder using pre-dried petroleum jelly in the Ar-filled glovebox. Rietveld refinement of XRD patterns was performed with the Topas 3 software provided by Bruker AXS.

Table 7 Calculated and measured nano-effects (ΔH(exp) nano, kJ mol⁻¹) without considering the influence of the oxide shell on the nano-particles

| Metal | A_BET (m² g⁻¹) | M (g mol⁻¹) | σ_{a,H,T》，} J m⁻² | ΔH_{exp} nano eqn (1) | ΔH_{exp} nano experiment |
|-------|----------------|-------------|-------------------|----------------------|-------------------------|
| Cu    | 10.6 ± 0.4     | 63.55       | 1.93 ± 0.19       | −1.3 ± 0.2           | −17.8 ± 0.8             |
| Ni    | 10.2 ± 0.4     | 58.69       | 2.36 ± 0.23       | −1.4 ± 0.2           | −3.5 ± 0.3              |

Table 8 Parameters to calculate the excess nano heat effect ΔH(exp) nano (kJ mol⁻¹) by eqn (4)–(7) and (9)²

| Metal | A_BET (m² g⁻¹) | M (g mol⁻¹) | βx | M (g mol⁻¹) | ρD (g cm⁻³) | σ_{a,H,T》，} (J m⁻²) | σ_{β,H,T》，} (J m⁻²) | σ_{αβ,H,T》，} (J m⁻²) | T (K) | ΔH_{exp} (kJ mol⁻¹) | ΔH^D (kJ mol⁻¹) |
|-------|----------------|-------------|----|-------------|--------------|---------------------|---------------------|---------------------|------|------------------|----------------|
| Cu    | 10.6           | 63.55       | 0.5| 71.55       | 6.0          | 1.93                | 0.7                 | 1.93                | 873  | 60.00            | −71.05         |
| Cu    | 10.6           | 63.55       | 0.5| 71.55       | 6.0          | 1.93                | 0.7                 | 1.93                | 1073 | 8.40             | −75.01         |
| Ni    | 10.2           | 58.69       | 1  | 74.69       | 7.45         | 2.36                | 0.9                 | 2.36                | 873  | 13.96            | −61.84         |
| Ni    | 10.2           | 58.69       | 1  | 74.69       | 7.45         | 2.36                | 0.9                 | 2.36                | 1073 | 18.208           | −64.33         |

² Density is from ref. 39, interfacial energies are from ref. 35 and 40, and enthalpy data are from ref. 41.
The energy-dispersive X-ray (EDX) detector signal for SEM analysis was calibrated using pure elements as standard materials and Co for the energy calibration.

The Ni and Cu nanoparticles were characterized by XRD analysis (XRD; Bruker D8 Advance X-ray diffractometer) and transmission electron microscopy (TEM; analytical TECNAI F20 field emission TEM). A silicon single crystal sample holder with a matching polymer (polycarbonate) cap was used in order to avoid a possible oxidation of NPs. The EDX mapping of NPs was performed with an energy-dispersive X-ray detector (EDAX TEAM Apollo XLDTW SDD).

The surface area of the nanopowders was estimated using the BET technique, whereby \( \text{N}_2 \) adsorption–desorption isotherms of the nanopowders were analyzed using a TriStar II 3020 instrument (Micromeritics). This method is based on a theory developed by S. Brunauer, P. Emmett and E. Teller where the name of the theory was taken from the first letter of each author’s surnames. According to this method, the surface area of a known mass of a sample was determined by monitoring the mass change by adsorption of nitrogen over time, which is widely used due to its availability in high purity and its strong interaction with most solids. The data collected during the measurement are shown in the form of a BET isotherm, which plots the quantity of gas adsorbed as a function of the relative pressure.

**Conclusions**

The presented experimental results show clearly that an extra exothermic heat effect (nano-heat effect) is observed when bulk pieces are replaced by nano-particles in drop calorimetric measurements. First of all, this is due to the loss of the large surface area of the nano-particles upon their dissolution. However, when the nano-particles are covered with a surface oxide shell, resulting in an exothermic chemical reaction with the solvent (a liquid alloy in the present case), the measured nano-effect can become even more exothermic, especially if the reaction enthalpy is strongly negative. This effect has been examined here on the example of the core/shell Cu/Cu\(_2\)O and Ni/NiO nano-particles dropped into Sn-rich liquid alloys.

**Conflicts of interest**

There are no conflicts to declare.

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