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Experimental investigation and thermodynamic reassessment of the ternary copper-nickel-lead system

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Abstract

Due to their high corrosion resistance and thermal stability, Cu-Ni-alloys have essential role in many materials engineering applications. Lead is an alloying element in these alloys although it may also be considered as an impurity in certain cases. In copper rich alloys, lead tends to diffuse into the grain boundaries and weaken the hot-working properties. In addition to alloys design, accurate knowledge of phase relations and solubilities in the ternary Cu-Ni-Pb system has important role in improving the copper and nickel smelting and refining processes.

In the present work, an isothermal equilibration technique was used to measure the mutual solubilities of liquid lead and solid CuNi foil in the temperature range 1280-1530 K. The samples were equilibrated and an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) and an Electron Probe Micro Analyzer (EPMA) were used to quantify the chemical composition of the phases. Selected solubility data obtained in this work were combined with the literature data to obtain a thermodynamic description of the Cu-Ni-Pb ternary liquid and fcc solid solution phases by applying the CALPHAD method. The ternary assessment agrees well with the experimental observations in this work.

Keywords: Cu-Ni-Pb, equilibration, solubility, CALPHAD, thermodynamic assessment

1. Introduction

Cupronickel (Cu-Ni) alloys are of great importance in numerous domestic and industrial scale applications due to their high corrosion resistivity and thermal stability [1]. Lead is an alloying element in many cupronickel alloys although it may also be considered as an

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impurity in some conditions. Lead has low solid solubility in both copper and nickel. In copper rich wrought alloys, lead has a tendency to diffuse into the grain boundaries and weakens the hot-working properties [1]. Cast alloys with high lead content are used for machining because lead in this case acts as an excellent lubricant resulting in less energy consumption for machining [1]. The ternary systems Cu-Ni-Pb is also of great importance owing to the recent European Union legislation changes as contained in the COST 531 project [2]. This legislation forbids continual usage of lead in fabrication of electronic or electrical components. In response to this challenge, COST 531 determined to understand thermodynamic properties of lead-free solder materials. Therefore, the ternary system Cu-Ni-Pb and its binaries are of great import to achieving this goal. In addition to alloys design, understanding the Cu-Ni-Pb phase diagram is also important in controlling copper and nickel smelting and refining processes. In this case, lead is considered as an impurity coming from the raw materials.

The CALPHAD method [3,4] uses simple systems (binaries and ternaries) to build multicomponent databases, which enables calculations of phase diagrams and thermodynamic properties of a specific system. Thermodynamic modelling can help to reduce the amount of experimental work needed. However, before this is achieved, accurate experimental data is needed as an important part of database development and validation work. A thermodynamic description of any system is largely as accurate as the experimental data used in the assessment.

Thermodynamic databases are built from lower to higher order systems. In this work, because of the lower order binary systems Cu-Pb and Ni-Pb have previously been re-assessed with new solubility data [5,6], there was a need to re-assess the Cu-Ni-Pb ternary system too. The Cu-Ni-Pb ternary phase diagram has been re-assessed according to the available experimental information in the literature and the selected equilibration experimental results obtained in this work. This work is a part of a larger development project in which a lead-based database is being developed as a subset of a larger metal-oxide-sulfide database (MTOX) [7,8].

2. Literature data

According to the SGTE Pure Element Transition Data [9,10], the melting points for pure Cu, Ni, and Pb are 1357.77 K, 1728.30 K, and 600.612 K, respectively. According to IPTS-68 [11] and ITS-90 [12], the freezing point of copper, nickel and lead are 1357.77 K, 1727.973 K, and 600.612 K, respectively. The crystal lattice structure for Cu, Ni and Pb is FCC_A1 from room temperature to their respective melting point. Lead has a high vapor pressure and its boiling point at 1 atm is 2022 K.

2.2 The Cu-Pb binary system

The Cu-Pb phase diagram consists of a liquid phase with a miscibility gap, a monotectic reaction, a eutectic reaction with no intermediate phases and very small solid solubility at
both ends. The Cu-Pb binary system assessment used in this study is based on the work by Vaajamo et al. [5], where solubility experiments and literature data were used to re-assess the thermodynamic interaction parameters for the system. The Cu-Pb phase diagram calculated from the parameter set reported in [5] is shown in Fig. 1.

![Cu-Pb phase diagram](image)

**Fig. 1.** The calculated Cu-Pb phase diagram based on the thermodynamic parameters reported in [5].

### 2.1 The Ni-Pb binary system

Similar to the Cu-Pb system, the Ni-Pb phase diagram consists of a liquid phase with a miscibility gap, a monotectic reaction, an eutectic reaction with no intermediate phases and very small solid solubility at both ends. The liquid miscibility gap is slightly larger than that of the Cu-Pb system and the lead solid solubility in solid nickel is smaller than in copper. The Ni-Pb binary system is based on the assessment by Vaajamo et al. [6], where solubility experimental results and literature data were used to re-assess the interaction parameters of the liquid and fcc solid solution phases. The Ni-Pb phase diagram calculated from the parameter set reported in [6] is shown in Fig. 2.
2.3 The Cu-Ni binary system

The Cu–Ni binary system has been studied by several authors. The latest assessment was done by Mey [13]. Contrary to the conflicting reports in the literature and an attempt to synthesize compounds at high-pressure conditions, no intermediate or ordered phases are observed in the Cu-Ni system [14]. However, various alloying reactions between Cu and Ni were experimentally observed by many researchers [15,16,17,18,19,20,21,22].

The Cu-Ni phase diagram comprises two equilibrium phases: the liquid phase and the fcc solid solution. The solidus and liquidus boundaries have a characteristic lens shape with a narrow two-phase region, as shown in Figs. 3 and 4. The solidus and liquidus boundaries are experimentally studied by several researchers [23,24,25,26]. The solid phase region constitutes a stable and wide miscibility gap, which is not very well established, as shown in Fig. 3. There are large deviations among the available experimental data [27,28,29,30,31] for the solid phase region. This large deviation could be due to the slow kinetics in the low-temperature region. Each of the available experimental data is superimposed on the calculated phase diagrams shown in Figs. 3 and 4.

According to Chakrabarti et al. [14], at a critical temperature ($T_c$) of 627.55 K and composition of 67.3 at. % Ni, the fcc phase decomposes into two phases, $\alpha_1$ and $\alpha_2$, and at
temperatures lower than $T_c$, $\alpha_2$ changes from a paramagnetic to a ferromagnetic state. The curie temperatures of Cu-Ni alloys were experimentally studied by [32,33,34,35,36,37]. The accepted curie temperature line, after the review of Chakrabarti et al. [14], is projected on the calculated phase diagram shown in Fig. 3. The experimental study of Kravetsa et al. [38] on thin films of Cu-Ni alloys has also resulted in similar low-temperature phase relations. However, owing to the differences in the thermodynamic properties of thin films and bulk materials [39], their determined curie temperatures are slightly higher. The latest study by Teeriniemi et al. [40], using the first-principles method, resulted in $T_c = 662$ K, at a composition of 78 at.% Ni, which is also higher than the previously suggested critical $T_c$ and composition values of [14]. In contrast, Turchanin et al.’s [41] assessment shifts the critical point to lower values, $T_c = 606$ K and $x_{Ni} = 59$ at.%. Recently, Xiong et al. [42] recommended that the SGTE values of $T_c$ and magnetic moment ($\beta$) for fcc Ni needs to be revised; the $\beta$ for fcc Ni seems to be underestimated, $T_c$ overestimated. Lattice stability of pure Ni in the SGTE compilation also needs to be modified, which is a valid recommendation.

In the present work, the parameter set with the magnetic contribution for the Cu-Ni system were taken from the MTOX database [7,8], version 7.0, without modifications. The thermodynamic interaction parameters of the liquid and fcc phases are based on the data of Mey [13]. The SGTE unary data [9,10] were used for the pure elements also without modifications.

**Fig. 3.** The calculated Cu-Ni phase diagram, with superimposed experimental data compiled in this study. The thermodynamic parameters were not assessed in this study, but taken from the MTOX database [7,8], version 7.0.
An enlarged view of the calculated liquidus and solidus boundaries, with superimposed experimental data compiled in this study. The thermodynamic parameter set was not assessed in this study, but taken from the MTOX database [7,8], version 7.0.

2.4 The Cu-Ni-Pb ternary system

Despite the fact that Cu-Ni-Pb can be regarded as a common alloy, there is only limited experimental information available in the literature about the system. Thermodynamic assessments of the system Cu-Ni-Pb have been reported by Wang et al. [43] and Miettinen et al. [44]. The assessments are based on phase diagram data in the literature. No experimental thermodynamic data is available in the literature for the ternary Cu-Ni-Pb system. Compilation of the ternary Cu-Ni-Pb system has been published by Villars et al. [45], Chang et al. [46], Hofmann [47] and Guertler et al. [48].

The first experimental work was published by Parravano and Mazzetti [49]. Later Guertler and Menzel [50] investigated the miscibilities in the Cu-Ni-Pb alloys. They noticed that the liquid miscibility gaps of the binary systems Cu-Pb and Ni-Pb extend only slightly, subsequently constituting a uniform structure. The experimental temperature remained unclear. Subsequently, Guertler and Menzel [51] also reported experimental data.
in the Cu-Ni-Pb system. They investigated the liquidus projection of two sections in the Cu-Ni-Pb ternary system 1) from Pb:Ni = 1.5 to Pb:Cu = 1.5 and 2) from Cu:Ni = 3 to pure Pb (Molar ratios). Nemilov and Strunina [52] investigated five sections of the system with Brinell tests and thermal and microstructure analyses. Pelzel [53] studied Ni-Pb, Cu-Pb and Cu-Ni-Pb systems by measuring the “thermal effect” from high to low temperatures. This enabled them to determine of the liquidus of different alloys containing 50, 60, 70 and 80 at. % Pb as well as Cu rich alloys with different Cu:Ni ratios. Quenching of the samples were slow and the equilibration time and the atmosphere during the experiments remain unclear. Szkoda [54] conducted X-ray and metallographic experiments of from which the liquidus projection of two sections of the ternary Cu-Ni-Pb system could be deduced. The results were partially similar to those reported in the work of Guertler and Menzel’s [51]. He determined roughly the extension of the liquid miscibility gaps of the binary systems Cu-Pb and Ni-Pb in the ternary Cu-Ni-Pb system.

3.1 Materials

The materials used were lead powder (Alfa Aesar 99.999 %, 0.6-3.0 mm) and metallic CuNi foil (Alfa Aesar Cu67/Ni33, 0.51 mm). EPMA analysis of the CuNi foil shows minor compositional variations in the matrix, which implies some level of inhomogeneity of the foil. However, considerable amount of the foil was used for each experimentation. About 0.6 – 0.9 g of CuNi foil was used for a 2 g of lead granule as a sample material in each experiment. The experiments were executed in evacuated quartz ampoules. The sample materials were placed in the ampoules and the argon flushed, evacuated and finally sealed.

3.2 Experimental method

3.2.1 Equilibration

The experimental method employed for investigating the Cu-Ni-Pb system has been reported in [6]. The experiments were performed in a vertical tube furnace (Lenton LTF 16/450). Temperature measurement was done using an S-type thermocouple, and using Keithley 2000 and 2010 voltmeters. The thermocouple was calibrated using copper, tin and ice water and gave maximum error of ±1.4 K. The ambient room temperature measurement was done with a Pt100 sensor (Platinum Resistance Thermometer). The sensor was calibrated against ice water at 273.15 K and the obtained resistance value was $R_0 = 100.017 \, \Omega$. This value was entered into NI LabVIEW temperature logging program. The manufacturer reported that the tolerance of the sensor was in accordance with the DIN IEC 751 standard B1/10 and an accuracy of ±0.03 K can be expected. The equilibration time was 48 h. The vertical tube furnace was built on a special stand with flexible handles, which enabled turning the furnace 180°, as shown in Fig. 5. This enabled easy handling of the samples. After quenching in cold (icy) water, the sealed ampoules which contained the sample materials were broken and the compositions of the saturated metals were analyzed.
3.2.2. Chemical analysis

The lead matrix samples were analyzed using an ICP emission spectrometer. The solubility of nickel and copper in liquid lead was analyzed with a Spectro Arcos Side on Plasma (SOP) instrument at Norilsk Nickel Harjavalta Oy, Finland. The lead solubility in the CuNi foils were analyzed by the Wavelength Dispersive Spectrometry (WDS) using a Cameca SX100 electron probe micro analyzer (EPMA) at the Geological Survey of Finland (GSF).

During quenching process, droplets of non-dissolved lead observed to be attached to the surface of the copper-nickel foil. This sticking of lead droplets on the surfaces of the foil complicated the EPMA analysis. Lead is soft and tends to spread and overlay the cross section of the sample during grinding and polishing. For this reason, the analysis points were selected such that areas with pure lead could be excluded.

During the ICP analysis, the whole sample was dissolved to avoid any errors due to segregations during quenching. Samples for EPMA analysis were mounted in resin, ground and polished to reveal the cross-section. For each sample, two six-point profiles were analyzed using galena as a standard for lead.
Trace analyses were carried out using a 25 kV accelerating voltage and a 500 nA beam current. The measurement time for Pb Lα was 600 s on peak and 300 s for background (both sides). Pb Lα was measured simultaneously with two spectrometers using LIF-crystal. This procedure gave a detection limit of 0.0076 wt.% for Pb. Pure metals were used as standards, adopting ZAF correction by Cameca for the raw data.

3.2.3. Diffusion time

The diffusion of copper and nickel in liquid lead has been discussed in previous research [5,55]. The experimentally obtained saturation points of nickel in liquid lead, reported in the literature [55] were in agreement with other experimental data. It was concluded that 48 h was sufficient time to reach equilibrium. The time required in the equilibration experimental studies of [51,53] was not reported. Nemilov and Strunina [52] reported 1 h equilibration time for their experiments before cooling down their samples.

Diffusion of lead in solid nickel has not been investigated previously. In Ref. [5] the diffusion of lead in solid copper was discussed with 48 h concluded to be sufficient time to reach equilibrium. In addition, according to [56] 48 h is enough to reach equilibrium. Even though, the diffusion of lead in the current CuNi foil might be expected to be slower than in a pure 0.1 mm Cu foil, it should not be far from the 48 h equilibration time. It was assumed that the concentration profiles obtained by EPMA would reveal if equilibrium was not reached in that they would show a clear parabolic shape indicating lower concentration in the middle of the sample. In the current work, the samples were thoroughly mixed during the experiments to facilitate faster diffusion. Although EPMA data had scatter, no compositional gradients were observed.

3.3. The experimental results

The results of the ICP and EPMA analysis along with the uncertainties of measurements are given in Table 1. The uncertainty of the temperature measurement was calculated by expanded uncertainty with coverage factor \( k = 2 \), taking into account the standard deviation of the temperature measurement, the calibration of the thermocouple and the uncertainty of the Pt100 sensor. The EPMA analyses obtained are calculated as average values of the profile points and the uncertainties as the calculated standard deviations of the profile points. The uncertainties of the ICP analyses were done by the company along with the analysis results and were not calculated by the authors. As mentioned in section 3.1, the purity of the current CuNi foil was low with high iron content and other impurities. In addition, the foil was observed to be inhomogeneous, which may have inflicted scattered results. This was also taken into account when comparing the experimental results with other published data. When taking into account the impurity of the CuNi foil used in the current experiments, the uncertainties of the chemical analyses are much larger than reported in Table 1. Due to the scattered results, CuNiPb2 and CuNiPb5 marked with * were excluded from the optimization.
When studying the purity of the sample materials of the other studies; Guertler and Menzel [51] used “originally melted lead, electrolytic copper and chemically cleaned nickel” in their experiments, Nemilov and Strunina [52] used electrolytic copper and nickel, and Pelzel [53] electrolytic copper, “Mond nickel” and fine lead. None of the authors reported the purity level of their starting materials.

Table 1
Results for Cu-Ni-Pb alloys in the vertical tube furnace along with their uncertainties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature °C</th>
<th>Temperature K</th>
<th>Pb in CuNi(s) (EPMA) wt.%</th>
<th>CuNi in Pb(I) (ICP) wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuNiPb1</td>
<td>1010.0±3.7</td>
<td>1283.1±3.7</td>
<td>0.472±0.077</td>
<td>3.8±0.2</td>
</tr>
<tr>
<td>CuNiPb2*</td>
<td>1057.2±3.5</td>
<td>1330.4±3.5</td>
<td>0.211±0.022</td>
<td>2.2±0.1</td>
</tr>
<tr>
<td>CuNiPb3</td>
<td>1157.9±3.5</td>
<td>1431.1±3.5</td>
<td>0.343±0.130</td>
<td>12.4±0.6</td>
</tr>
<tr>
<td>CuNiPb4</td>
<td>1208.8±3.7</td>
<td>1482.0±3.7</td>
<td>0.299±0.072</td>
<td>8.5±0.4</td>
</tr>
<tr>
<td>CuNiPb5*</td>
<td>1257.2±3.7</td>
<td>1530.3±3.7</td>
<td>0.343±0.104</td>
<td>7.6±0.4</td>
</tr>
</tbody>
</table>

* Not used in the assessment

Thermodynamic models

4.1 Pure elements

The temperature dependence of the molar Gibbs energy of a phase, i, with fixed composition, for pure elements in a specified lattice structure, is commonly written using an expression of the type shown in Eq. (1).

\[ \Delta G_i(T) - H_i^{SER}(298.15 \text{ K}) = a + bT + cT\ln T + dT^2 + eT^3 + f/T + \sum g_n T^n \]  

where \( a…f \) are a standard set of six coefficients obtained by assessing and fitting measured thermodynamic properties of the element and phase in question. Further coefficients \( g_n \) are sometimes added if required. The difference in Gibbs energy between a phase and a reference phase with the same elemental composition (lattice stability) can be calculated by subtracting one set of assessed coefficients from another.

The reference state for enthalpy adopted currently, and within SGTE, is that of the elements in their stable forms at 298.15 K and 1 atm pressure, denoted by the superscript SER. Coefficients for pure elements, also called unary data, have been derived by SGTE and reported by Dinsdale [9]. Values used in the current study are presented in Appendix A, Table A.1.

4.2 Liquid phases

The liquid and fcc phases were considered as substitutional solutions, allowing complete mixing of copper, nickel and lead. Their thermodynamic excess functions were fitted using Redlich-Kister polynomials [57], to model the excess integral Gibbs energy, \( \Delta G \), which in a general form, for a ternary system, can be written as
\[ a^\alpha G = x_i x_j \sum_{n=0}^m n L_{ij}(x_i-x_j)^n + x_i x_k \sum_{n=0}^m n L_{ik}(x_i-x_k)^n + x_j x_k \sum_{n=0}^m n L_{jk}(x_j-x_k)^n + x_i x_j x_k (L_{ij;k} + x_j L_{ij;k} + x_k^2 L_{ij;k}) \]  

(2)

where \( n L_{ij} \) and \( L_{ijk} \) respectively, are temperature dependent binary and ternary interaction parameters, to be estimated based upon experimental data. In the current work each is a linear function of temperature, for example \( n L_{ij} = n L_{ij}^0 + n L_{ij}^1 T \). \( m \) is the order of the polynomial for each binary system. \( x_i, x_j, x_k \) are the mole fractions of the components Cu, Ni, Pb in the phase.

The magnetic transformation of pure Cu and Ni at the magnetic transition temperature is described using the model introduced by Inden [58] and modified by Hillert and Jarl [59]. As mentioned in section 2.3, the magnetic properties of copper, nickel and copper-nickel were not modified in the current work. Values from the unary [9,10] and MTOX-databases [7,8], presented in Appendix A, Table A.2, were used without change.

5. Optimization

Optimization was carried out with MTDATA software version 5.10 [60]. The Unary-database values [9,10] were used for the pure components. The model parameters of the alloy phases were obtained from equation (2), and the experimental data were fitted by a least squares method.

The Cu-Pb and Ni-Pb binary systems interaction parameters were taken from literature [5,6]. The Cu-Ni binary system interaction parameters were taken from the MTOX database version 8.0. [7,8], which are based on the assessment by Mey [13]. The thermodynamic interaction parameters are presented in Appendix A1, Table A2.

The optimization of thermodynamic interaction parameters of the Cu-Ni-Pb ternary system is based on the experimental data of [48,52,53] and this study. After pre-optimization steps, all the data were given a 20 K temperature uncertainty and 1 as weighting coefficient. The CuNiPb2 and CuNiPb5 data presented in Table 1 were excluded from the assessment due to high scattering. The values by Nemilov and Strunina [52] were considered as the most accurate, with an exception of one of their experimental data point (67.84 at.%Pb, 14.89 at.% Cu, 17.28 at.% Ni at 1217.15 K) was excluded, because it was dragging the lead rich liquidus into a too low temperature zone, as show in section 6, Figs. 8 and 11. The experimental values by Guertler and Menzel [51] were given a higher uncertainty because the points were digitized from the graphics. Moreover, they did not report the equilibration time or the quenching methodology used. Although their reported purity of copper and nickel they used was high, the purity of lead remains unclear. This was also observed in Pelzel [53]. In his experiments, it is reported that the samples were quenched slowly, which probably resulted in lower nickel content. This would explain the discrepancy between the calculated liquidus lines and his experimental points shown in the next section in Fig. 13.
6. Results and discussion

The thermodynamic interaction parameters for the liquid and fcc solution phases optimized in this study are listed in Table 2 together with the parameter sets reported previously by Miettinen et al. [44] and Wang et al. [43]. According to these results, lead dissolves preferentially into solid copper-nickel than in solid nickel.

Table 2

Optimized thermodynamic interaction parameters for the system Cu-Ni-Pb obtained in this study and reported previously by [43,44]. The parameters are in J·(mol·atom)^{-1}, J·(mol·atom)^{-1}K^{-1} and temperature in K.

<table>
<thead>
<tr>
<th></th>
<th>This work</th>
<th>Mietinen et al. [44]</th>
<th>Wang et al. [43]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Ni-Pb (Liquid)</td>
<td></td>
<td>Cu-Ni-Pb (Liquid)</td>
<td>Cu-Ni-Pb (Liquid)</td>
</tr>
<tr>
<td>(0L_{CuNiPb}^{liq})</td>
<td>615.00 - 0.0006(\cdot T)</td>
<td>(0L_{CuNiPb}^{liq}) = 210000 - 200(\cdot T)</td>
<td>(0L_{CuNiPb}^{liq}) = 244630 - 200(\cdot T)</td>
</tr>
<tr>
<td>(1L_{CuNiPb}^{liq})</td>
<td>27.9427 + 0.0014(\cdot T)</td>
<td>(1L_{CuNiPb}^{liq}) = 515000 - 340(\cdot T)</td>
<td>(1L_{CuNiPb}^{liq}) = 114881.91 - 66.67(\cdot T)</td>
</tr>
<tr>
<td>(2L_{CuNiPb}^{liq})</td>
<td>-21085.02 + 0.0057(\cdot T)</td>
<td>(2L_{CuNiPb}^{liq}) = 210000 - 200(\cdot T)</td>
<td>(2L_{CuNiPb}^{liq}) = 223405.59 - 188.33(\cdot T)</td>
</tr>
<tr>
<td>Cu-Ni-Pb (FCC_A1)</td>
<td></td>
<td>Cu-Ni-Pb (FCC_A1)</td>
<td></td>
</tr>
<tr>
<td>(0L_{CuNiPb}^{fcc})</td>
<td></td>
<td>(0L_{CuNiPb}^{fcc}) = 100000</td>
<td></td>
</tr>
<tr>
<td>(1L_{CuNiPb}^{fcc})</td>
<td>-39999.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2L_{CuNiPb}^{fcc})</td>
<td>-39999.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6 compares the EPMA results of the current study with calculations based on assessed thermodynamic parameters. It takes the form of a temperature-composition section starting from a composition with ratio Cu:Ni=0.2 to which up to 1 at.% Pb was added. EPMA results from the current study, showing the maximum solubility of lead in solid copper-nickel (fcc) alloys, were superimposed on the calculated phase boundaries. The experimental points show discrepancy, especially at lower temperatures. In this optimization, the calculated phase boundary is an average of the experimental points, which is probably closest to the reality.

Fig. 7 presents a comparison of the ICP analyses in the current study with calculated phase boundaries. The starting points are different Cu:Ni ratios with additions up to pure lead. In both Figs. 6 and 7 the experimental points with tails were not used in the optimisation due to high scattering. The point Cu:Ni =1 in Fig. 7 shows good agreement with the calculated phase boundary but the rest of the points are at much higher temperature.
Fig. 6. A $T$ vs. $x$ section starting from Cu:Ni=0.2 and covering addition of up to 1 at.% Pb. The experimental values superimposed on the diagram are the EPMA measurements in this study. The two experimental points with tail were not used in the optimization.

Fig. 8 shows a calculated isopleth starting with composition ratio of Cu:Ni=1.00 with addition of up to pure lead. The experimental points of Nemilov and Strunina [52] are superimposed on the figure showing very good agreement with one experimental point obtained in this study (Cu:Ni=1.00). The binary and ternary parameter sets by Miettinen et al. [44] and Wang et al. [43] were used to calculate the phase boundaries and are compared with this study. As shown in the Fig. 8, the liquidus lines calculated based on the parameter sets of [43,44] are lower than those obtained in this study. This is probably due to the experimental point at 67.84 at.% Pb and at 1217 K reported by [52], which draws the liquidus line towards low temperature. This is shown more clearly in Fig. 9, which presents an isotherm at 1217.15 K, excluding experimental points of [52]. Fig. 9 is based on the parameter sets in the current study, Miettinen et al. [44] and Wang et al. [43]. This figure shows that the liquidus line does not extend to such low temperature.
Fig. 7. A $T$ vs. $x$ section starting from different Cu:Ni ratios and covering addition up to pure lead. The experimental values superimposed on the diagram are ICP measurements in this study. The two experimental points with tail were not used in the optimization.

Fig. 8. The calculated isopleth of the Cu-Ni-Pb ternary system with experimental points by [52] starting with Cu:Ni=1 and ending to pure lead. The solid line refers to this study, dotted lines (····) refer to the parameter set by [44] and dashed lines (- - -) refer to the parameter set by [43].
Fig. 9. An isotherm at 1230 K calculated with the parameter sets in this study, Miettinen et al. [44] and Wang et al. [43]. The experimental points reported by Nemilov and Strunina [52] were not included in the assessment made in this study.

Fig. 10. Two calculated isopleths of the Cu-Ni-Pb system with starting compositions of Cu:Ni = 0.6 (higher) and Cu:Ni = 4.5 (lower) and ending composition of pure lead. The solid lines refer to this study, dotted lines refer to the parameter set by [44] and dashed lines refer to the parameter set by [43]. The experimental points by [52] are superimposed.
Fig. 10 shows two isopleths calculated from the parameter set of this study (solid line), Miettinen et al. [44] (dotted line) and Wang et al. [43] (dashed line). The calculations based on this study show a better agreement with the experimental points of Nemilov and Strunina [52] than the previous assessments of [43,44].

Fig. 11 shows a calculated isopleth with fixed composition of 60 wt.% Pb. The liquidus line increases from the starting point 40 wt.% Cu and 60 wt.% Pb towards the nickel rich end point (40 wt.% Ni). The solid line refers to the parameter set of this study, the dotted line refers to the parameter set of Miettinen et al. [44] and the dashed line refers to the parameter set of Wang et al. [43]. The calculations based on this study are showing a better agreement with the experimental points of [48,52,53] than assessments made previously.

![Fig. 11. An isopleth of the Cu-Ni-Pb ternary system starting with Cu:Pb=2:3 and ending with Ni:Pb=2:3. The solid line refers to this study, dotted line refers to the parameter set by [44] and dashed line refers to the parameter set by [43]. The experimental points of [51,52,53] are superimposed. The Cu-rich side of the diagram is enlarged for clarity.](image)
Fig. 12 shows an isopleth starting from Cu: Ni = 3 to pure lead. The solid line refers to the parameter set of this study, the dotted line refers to the parameter set of Miettinen et al. [44] and the dashed line refers to the parameter set of Wang et al. [43]. The assessments of [43, 44] show better agreement with the experimental points of Guerler and Menzel [51], resulting in liquidus line that would be at slightly lower temperature than calculated with the parameter set of this study.

Fig. 13 compares the calculated liquidus lines based on the parameter sets in this study, Miettinen et al. [44] and Wang et al. [43] together with the experimental points of Pelzel [53]. The experimental points reported by Miettinen et al. [44] is the closest to the values obtained in this study. However, none of the calculated phase boundaries are close to the experimental points at higher lead contents. This might be the reason Pelzel [53] used slow quenching in his experiments, probably resulting in nickel precipitation from the melt.

![Fig. 12. The calculated isopleth of the Cu-Ni-Pb ternary system with experimental points by [51] starting with Cu: Ni = 3 and ending to pure lead. The solid line refers to this study, the dotted line refers to the parameter set by [44] and the dashed line refers to the parameter set by [43].](image-url)
Fig. 13. The calculated liquidus lines of the Cu-Ni-Pb ternary system with different lead compositions 0, 10, 20, 30, and 38 wt.% Pb as a function of temperature and nickel composition (wt.%). The experimental points by Pelzel [53] are superimposed in the figure. The solid line refers to this study, the dotted line refers to the parameter set by [44] and the dashed line refers to the parameter set by [43].

7. Summary and conclusions

Thermodynamic assessment for more accurate descriptions of systems require a combination of good experimental data and a thorough assessment. However, good experimentation presents several challenges, which must progressively be overcome as more information on the systems are acquired. An experimental study of the Cu-Ni-Pb system as observed in this research is currently challenging. Based on the combined experimental and thermodynamic study of the ternary system Cu-Ni-Pb, the following can be inferred:

i. The MTOX database [7,8] has been extended with the Cu-Ni-Pb ternary system. This has been achieved through previously assessed binary Cu-Pb and Ni-Pb systems. The Cu-Ni binary system parameter set was taken from the MTOX
The study has revealed that although the Cu-Ni system is well known at high temperatures, the solid phase region constituting a miscibility gap is not very well established.

ii. Owing to the limited experimental data of the ternary Cu-Ni-Pb system, this study focused on measuring the mutual solubilities of solid copper-nickel foil and liquid lead. On account of impurities found only selected experimental data were used in the assessment. However, this is the first attempt at experimentally measuring solid solubility of lead in copper. Moreover, even though the data is scarce, this study provides information on the order of magnitude of the solubility.

iii. The two fold challenge from this study was lack of adequate experimental data in literature as well as the limitations of methods used to conduct the experiments. In the literature, the values of Nemilov and Strunina [52] and Guertler and Menzel [51] were considered as the most accurate and the agreement between their experimental points and the phase boundaries calculated from the parameter set of this study is very good.

iv. In general, the Cu-Ni-Pb ternary system has large scatter in experimental data, which makes assessing challenging. In this research, several parameters were optimized by using binary assessments. The completed ternary assessment is in good agreement with the experimental observation in this study, which can be considered as the most accurate.

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