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Experimental investigation and thermodynamic re-assessment 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.

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 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 importance 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

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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.

2.1. 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.

2.2. 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.

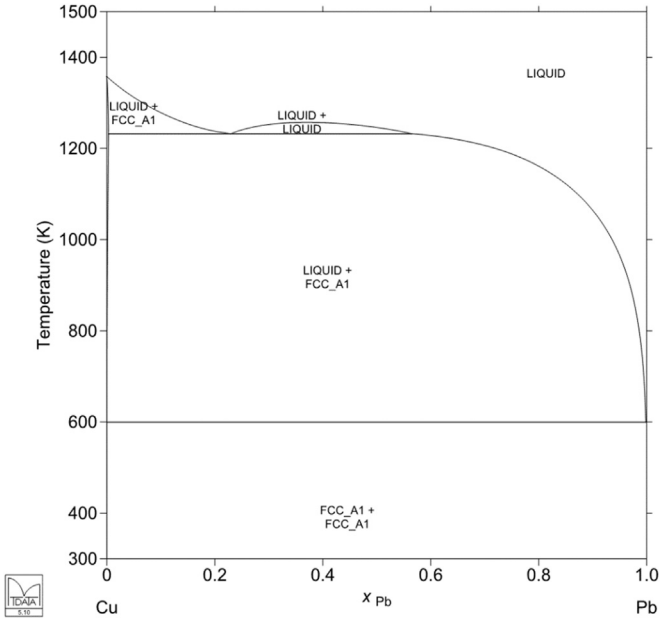

Fig. 1. The calculated Cu-Pb phase diagram based on the thermodynamic parameters reported in [5].

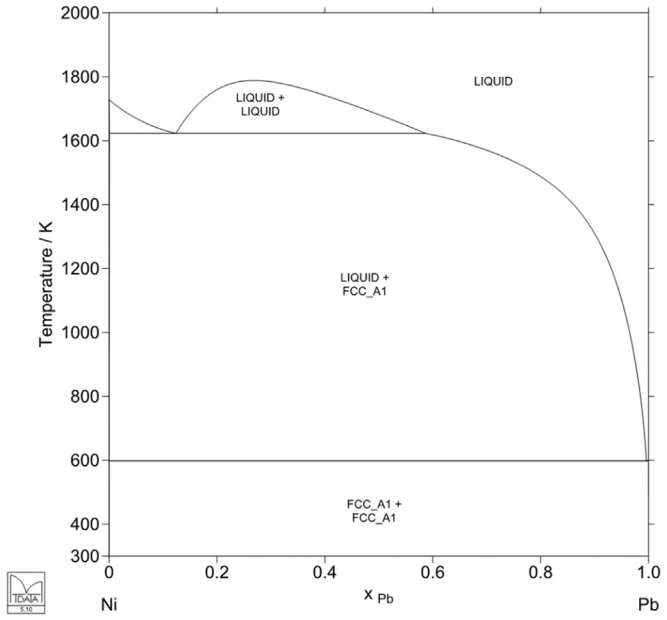

Fig. 2. The calculated Ni-Pb phase diagram based on the thermodynamic parameters reported in [6].

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 [15–22].

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 [23–26]. 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 [27–31] 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.

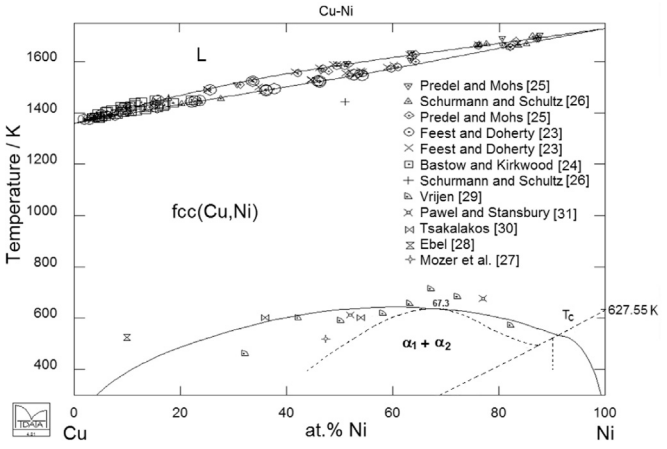

Fig. 3. The calculated Cu-Ni phase diagram, with superimposed experimental data compiled in this study. The thermodynamic parameters were not assessed in this study, but taken from the MTOX database [7,8], version 7.0.