Minerals Engineering 42 (2013) 68–75

Contents lists available at SciVerse ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Phase stabilities and thermodynamic assessment of the system Cu–Pb–S

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ARTICLE INFO

Article history:
Received 3 July 2012
Accepted 28 November 2012
Available online 11 January 2013

Keywords:
Thermodynamics
Phase relations
Cu_2S-PbS system
Cu–Pb–S system

ABSTRACT

An equilibration quenching technique was used to evaluate experimentally the phase relations in the Cu–Pb–S system between 763 and 1273 K. At 763–788 K, the formation of a ternary phase was confirmed. In addition, the thermodynamic properties of the Cu–Pb–S ternary system between 763 and 1573 K were critically assessed and optimized by the CALPHAD (CALculation of PHAse Diagrams) method, using the experimental results from this work and critically evaluated literature data. The obtained thermodynamic dataset allows the thermodynamic properties and phase equilibria in the Cu–Pb–S system to be calculated with good agreement to the experimental results. The effects of different process variables on the lead and copper distributions between the metal and matte can be calculated to improve the process control and economics.

1. Introduction

In copper manufacturing from sulfide concentrates, lead is considered a harmful impurity that must be eliminated from the product during processing because of its adverse effects on high-purity copper products used for electric and heat conductivity purposes. A large portion of lead from the feed material volatilizes in the copper smelting process, but the remaining part is dissolved, mainly into the matte, and it must be removed in the converting or the subsequent fire-refining step (Steinhauser et al., 1984).

Phase diagrams and thermodynamic information can be used in pyrometallurgy to provide a better understanding of the behavior of the process and their components during smelting and solidification. This information is essential for process development and improvement. The phase diagram data for sulfide liquids can also be used to evaluate sulfide ores (Naldrett, 1989).

Under copper production conditions phase diagrams can be used to evaluate the properties and sensitivity of different changes in the process to the liquid immiscibility gaps used to separate matte, white metal and blister copper. The information regarding the Cu–Pb–S system is especially useful in the converting process step, where lead as an impurity affects the equilibrium between blister copper and white metal.

The pseudobinary system Cu_2S–PbS has been described by Friedrich (1907), Graig and Kullerud (1968), Kobylov et al. (1976), Goto et al. (1983) and Johto (2009). The eutectic temperatures in these references are within the temperature range of 790–813 K and the experimental liquidus lines agree one another. The experimental studies of Friedrich (1907) and Johto (2009) have been performed with non-stoichiometric copper sulfides, which may cause errors in the results when expanding the quasibinary system to the ternary system Cu–Pb–S. Kobylov et al. (1976), performed an experimental study using copper (I) sulfides with three different sulfur contents, including stoichiometric Cu_2S.

At high temperatures three separate liquid domains have been determined in the Cu–Pb–S ternary system; the first contains over 98 wt.% sulfur, the second is a sulfide-rich matte containing 20–26 wt.% sulfur in the Cu–S join and 9–27 wt.% sulfur in the Pb–S join, and the third is a metal-rich solution containing less than 2 wt.% sulfur. Miscibility gaps exist between the sulfur-rich and sulfide-rich liquids, and between sulfide-rich and metal-rich liquids. The matte-metal miscibility gap has been investigated by Guertler and Meissner (1921), Guertler and Landau (1934), Graig and Kullerud (1968), Cho and Jun (1982, 1983), Cho et al. (1982), Goto et al. (1982, 1983) and Eric and Timucin (1989) over a temperature range of 1273–1523 K. The slope of the liquid immiscibility boundary is very steep on the matte side. The measured tie-line distributions and the phase boundaries in different references are generally congruent with one another.

The phase stabilities at temperatures below 1273 K have been determined in the works of Graig and Kullerud (1968), Goto et al. (1983), Cho and Won (1985) as well as Cho (1986). When lowering the temperature, the three phase zones in the system expand and the sulfide liquid domain shrinks, as it is a small four-sided area in the middle region of the PbS–Cu_2S join at 873 K. According to Graig and Kullerud (1968), the sulfide liquid remains stable down to 781 K, at which point the liquid phase undergoes a monotectic reaction forming solid PbS, a diginite solution and liquid sulfur.

The solid solubility of lead into diginite solution has been measured by Cho and Jun (1983), Goto et al. (1983), Cho and Won

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http://dx.doi.org/10.1016/j.mineng.2012.11.009

(1985) and Cho (1986). The maximum solubility in diginite measured by Goto et al. (1983) was approximately 10 at.% PbS at the eutectic temperature, whereas the other reported solubilities are generally lower. The solubility of copper in lead sulfide has not been reported.

At 801–803 K, Graig and Kullerud (1968) and Kobylov et al. (1976) have identified a ternary phase with a composition of $Cu_{14}Pb_2S_{9-x}$ (Graig and Kullerud, 1968) or $7Cu_2S{\cdot}2PbS$ (Kobylov et al., 1976) in the Cu_2S–PbS join. The ternary phase, named A (Graig and Kullerud, 1968), breaks down to liquid Pb, solid PbS and a diginite solution at 753–759 K. This ternary sulfide is the only ternary compound reported in the system Cu–Pb–S.

The distribution of small concentrations of lead in the sulfide matte and liquid copper has been investigated at different temperatures by Azuma et al. (1970) and Sinha et al. (1984). The measured values agree well with one another. The distribution coefficients between matte and copper, $L^{m/Cu}_{(Pb)} = (\%Pb)_{matte}/[\%Pb]_{copper}$ of 3.6 and 4.06 at 1405 K and 1505 K, respectively (Sinha et al., 1984).

The solubilities of sulfur and copper into liquid lead at 873 K have been investigated by Twidwell and Larson (1966), at 873–1173 K by Grant and Russell (1970) and at 823–1073 K by Michimoto et al. (2007). Twidwell and Larson (1966) as well as Grant and Russell (1970) measured the effect of copper on the activity of sulfur in metallic lead-copper alloys in equilibrium with hydrogen–hydrogen sulfide gas mixtures, obtaining excellent agreement. The error of these measurements is significant, especially at higher temperatures because of problems caused by the high vapor pressure of lead. Michimoto et al. (2007) performed equilibrium experiments with two different mixtures, both containing pure lead and a sulfurous mixture. Their results show a linear relationship between the logarithm of both sulfur and copper solubilities into liquid lead and the reciprocal absolute temperature. The experimental results of Michimoto et al. (2007) were extracted from the graphics, affecting the errors of these points used in this assessment.

The lead sulfide vapor pressure in the system Cu_2S–PbS has been measured by Nesterov et al. (1969) and Botor et al. (1990) at temperatures between 1042 and 1523 K using a transport method to determine the activity of lead sulfide in the liquid solution. The dew-point technique has been utilized to obtain the activities of lead sulfide in the liquid solution of the system Cu_2S–PbS from 1423 to 1523 K by Azuma et al. (1970) and Eric and Timucin (1981), and activities of lead in the liquid solution of the system Cu–Cu_2S–PbS–Pb from 1423 to 1523 K by Azuma et al. (1970) and Eric and Timucin (1989).

Nesterov et al. (1969) and Botor et al. (1990) reported that the PbS activity referred to PbS(l) over the entire measured composition range in the system Cu_2S–PbS exhibits negative deviation from Raoult's law. In contrast, the results of Azuma et al. (1970) show a positive deviation from the ideal PbS activity, referred to PbS(l), in the composition range of 0–30 at.% PbS and a negative deviation from ideal PbS activity in the composition range of 30–100 at.% PbS at all temperatures measured. With the activities of Pb referred to liquid Pb in the system Cu–Cu_2S–PbS–Pb, Azuma et al. (1970) and Eric and Timucin (1981) reported a slight deviation from Raoult's law.

2. Material and methods

In the phase diagram experiments, lead sulfide from Sigma–Aldrich (St. Louis, MO, USA) with a metal purity of 99.9 wt.% and copper (I) sulfide from Alfa-Aesar (Ward Hill, MA, USA) with a metal purity of 99.5 wt.% were used as starting materials. In the ternary phase equilibratia experiments, in addition to commercial materials, synthesized copper sulfide with a composition of $Cu_{1.83}S$ and lead sulfide with a composition of $Pb_{1.08}S$ were used. The 2 g samples were evacuated and sealed into fused quartz tubes (50 mm long and 7 mm inner diameter) that had been flushed with argon.

Table 1
Composition of the liquid phase in experiments confirming the achievement of equilibrium at 813 K.

Time	wt.% PbS	mol.% PbS
2	48.5	38.5
4	48.6	38.6
8	49.1	39.1
16	48.7	38.7
Goto et al. (1983)	49.5	39.5

The phase diagram equilibration experiments were carried out in a Lenton (Hope Valley, UK) UAF 16/10 chamber furnace. During the experiments, the furnace temperature was tracked with an S-type thermo-element connected to Keithley 2000 multimeter – data logger (Cleveland, Ohio, USA) and recorded with Agilent Vee software (Agilent Technologies, Santa Clara, California, USA), version 7.51. The samples were first melted at 1523 K and then cooled down to the equilibration temperature. After equilibration, the ampoules were quenched in an ice water mixture. The ternary phase experiments were carried out with a similar method but using a Lenton CSC 12/90/450 tube furnace. The overall accuracy of the temperature measurements was estimated as ±2 K.

The quenched ampoules were broken down, and the samples were cut in half lengthwise. These parts were used to prepare polished sections for SEM-EDS analysis using standard wet methods such that the cut surface from the center of the sample can be analyzed. The entire cut surface was examined to detect all phases present; oxide phases were of particular interest in terms of signaling sample oxidation. The compositions of the detected phases were analyzed using a LEO 1450 (Carl Zeiss Microscopy GmbH, Jena, Germany) scanning electron microscope with a Link Inca X-Sight 7366 Energy EDS- analyzer (Oxford Instruments plc,

Table 2
Experimental information used in the assessment, including types, uncertainties and weight factors.

Authors	Phase diagram information	Thermodynamic data	Uncertainty (%)	Weight factor
Kobylov et al. (1976)	×		3	1
Cho et al. (1982)	×		3	1
Cho and Jun (1982)	×		3	1
Cho and Jun (1983)	×		3	1
Cho and Won (1985)	×		3	1
Cho (1986)	×		3	1
Goto et al. (1983)	×		5	1
Eric and Timucin (1989)	×	×	2	1
Sinha et al. (1984)	×		2	1
Nesterov et al. (1969)		×	2	1
Botor et al. (1990)		×	1	3
Eric and Timucin (1981)		×	2	1
This work	×		1	3