Tellurium is an unwanted admixture in silver thus it is important to optimize tellurium removal from Ag by controlling its distribution between the liquid, slag and gaseous phases. Consequently, the knowledge of the state of thermodynamic equilibrium which determines the distribution of tellurium between these phases is very important. For its prediction it is necessary to know the thermodynamic description of every phase. In the present paper an attempt has been made to work out a thermodynamic description of the Ag-Pb-Te system. This description is based on literature information and the CALPHAD method. Then, the influence of lead on the vapor pressure of tellurium is analysed.

Keywords ternary phase diagram, thermodynamic modeling, vapor pressure

1. Introduction

During the electrolytic refining of copper a by-product known as anodic slimes is obtained and collected in anodic compartments. It is a valuable source of silver, gold, platinum group metals, but also it contains lead, bismuth, antimony, selenium and tellurium. The amount of tellurium in copper anode slimes has been reported to vary from 0.3 to 3%, though sometimes it can reach the level of 10%.\(^\text{[1,2]}\) It occurs principally in solid solutions, but, if the Te content is high enough telluride phases can also be formed.

After acid pretreatment the slime is melted under reducing conditions in a reverberatory furnace. The product of this so-called Kaldo process is an alloy containing mainly lead and silver with the additions of a number of solutes. This alloy is next oxidized and during this operation solutes are transferred into the slag phase. Noble metals remain in silver while selenium and some tellurium are removed after oxidation in the form of gaseous species. However, tellurium may still be present in silver. Needless to say, the amount of tellurium in silver exceeding 20 ppm lowers its price and results in difficulty of selling the silver on the market. It is thus important to optimize tellurium removal from silver by controlling its distribution between the liquid, slag and the gaseous phases. Consequently, knowledge of the state of thermodynamic equilibrium which determines the distribution of tellurium between these phases is very important. In the present paper an attempt has been made to work out a thermodynamic description of the Ag-Pb-Te system, and then to predict the influence of lead content in silver on the vapor pressure of tellurium in the gaseous phase.

2. Thermodynamic Description of the Phases

The following phases are considered in this work: FCC\(_A1\) (Ag, Pb), Hexagonal\(_A8\) (Te), liquid, PbTe, Ag\(_2\)Te, Ag\(_5\)Te\(_3\), Ag\(_65\)Te\(_{345}\). Detailed information about these phases is given in Table 1 and below.

2.1 Substitutional Solution—FCC\(_A1\) (Ag, Pb)

The Gibbs free energy of pure elements as a function of temperature \(^{0}G_i(T) = G_i(T) - H_i^{SER}\) is represented by Eq 1:

\[
^{0}G_i(T) = a + bT + cT \ln(T) + dT^2 + eT^{-1} + fT^3 + iT^4 + jT^7 + kT^{-9}
\]  
(Eq 1)

The \(^{0}G_i(T)\) data are referred to the constant enthalpy value of the standard element reference \(H_i^{SER}\) at 298.15 K and 1 bar as recommended by Scientific Group Thermodata Europe (SGTE).\(^\text{[1]}\) The reference states are: FCC\(_A1\) (Cu and Pb) and Rhombohedral\(_A7\) (Sb). The \(^{0}G_i(T)\) expression may be given for several temperature ranges, where the coefficients \(a, b, c, d, e, f, i, j, k\) have different values. The \(^{0}G_i(T)\) functions are taken from SGTE Unary (Pure elements) TDB v.4.\(^\text{[2]}\) Thermodynamic functions of pure elements are listed in Table 2. The FCC\(_A1\) phases are described by the regular solution model\(^\text{[3]}\):

\[
G_m(T) = \sum_i x_i^{0}G_i(T) + RT \sum_i x_i \ln(x_i) + \sum_i \sum_{j>i} x_i x_j \left( \sum_v v L_{ij}(x_i - x_j)^v \right)
\]  
(Eq 2)
where the $\sum_{i,j>i} x_i x_j (\sum_{k=1}^{\infty} I_{ij}(x_i - x_j))$ part is the Redlich-Kister polynomial for the excess Gibbs free energy.

2.2 Stoichiometric Compounds—PbTe, Ag₂Te, Ag₅Te₃, Ag₆₅₅Te₃₄₅

Binary stoichiometric compounds PbTe, Ag₂Te, Ag₅Te₃, Ag₆₅₅Te₃₄₅ are described as the line compounds using the following expression:

$$G_m(T) = a + bT + \sum_i x_i \text{GHSER}_i$$ (Eq 3)

The polymorphic transformations of the phases Ag₂Te, Ag₅Te₃, and Ag₆₅₅Te₃₄₅ were neglected since no available information about these transformations in the ternary system exists.

2.3 Associated Liquid Model

The liquid phase is described using the association model.[14] Since the enthalpy of mixing of the liquid phase exhibits V-shape in Pb-Te and Ag-Te systems the compositions of conglomerates were chosen to be PbTe and Ag₂Te. Apart from the shape of the enthalpy of mixing, the literature information proved the existence of the liquid associates in Ag-Te and Pb-Te systems. Dancy[5] and Faber[6] measured electrical conductivity of liquid Ag-Te and liquid Pb-Te alloys, respectively. From their work it is clear that liquid associates exist in these solutions. Moreover, Glazov et al.[7] showed that in the liquid Pb-Te alloy there exists a correlation between conductivity and viscosity. This also proves the existence of the liquid Pb-Te associates. The Gibbs energy for one mole of atoms is given by the following formula:

$$G_{m,\text{Liquid}} = \left[ x_{Ag} G_{Ag}^{\text{Liquid}} + x_{pb} G_{pb}^{\text{Liquid}} + x_{Te} G_{Te}^{\text{Liquid}} \right. + x_{Ag_{2}Te} G_{Ag_{2}Te}^{\text{Liquid}} + x_{pbTe} G_{pbTe}^{\text{Liquid}} + RT(x_{Ag} \ln x_{Ag} + x_{pb} \ln x_{pb} + x_{Te} \ln x_{Te} + x_{Ag_{2}Te} \ln x_{Ag_{2}Te} + x_{pbTe} \ln x_{pbTe}) \right] / (1 + 3x_{Ag_{2}Te} + 2x_{pbTe})$$ (Eq 4)

3. Experimental Information

Taking into account the associate solution model which was used in this work for description of the ternary Ag-Pb-Te system, one should mention that binary Pb-Te and Ag-Te systems had to be also remodeled. For reoptimization of these binary systems we used exactly the same experimental sets as in our previous works[8,9] where an ionic model was used. The binary Ag-Pb system was also recalculated using the same literature information as Lee et al.[10] used.

Experimental information about Ag-Pb-Te system is very limited. Enthalpy of mixing of the liquid phase was measured by Rommer and Blachnik.[11] They measured the heat of mixing for five sections: Te-Ag₅₀₅₀Pb₅₀₀₅, Te-Ag₆₀₅₀Pb₄₀₀₅, Te-Ag₅₀₅₄Pb₆₀₀₅, Te-Ag₄₀₅₆Pb₆₀₀₅, Te-Ag₄₀₅₆Pb₆₀₀₅. At temperatures: 973, 1073 and 1173 K. No information about either activities or chemical potentials of components in the ternary liquid alloys was found. The DTA information was provided by Blachnik and Gather[12] and Blachnik and Bolte.[13] Blachnik and Gather[12] investigated the cross-section Ag₃Te-PbTe. Besides DTA experiments they also identified the phases present in the system using x-ray and metallographic methods. Blachnik and Bolte[13] examined two isopleths in Ag-Pb-Te system. The first one is Ag₂Te-Pb section, and the second one is the PbTe-Ag section. Similarly, as in previous paper,[15] DTA, x-ray and metallographic methods were used for the determination of phase equilibria. Unfortunately, the isopleths don’t agree with each other. In the cross point of the two isopleths a difference between liquidus temperatures is about 100°. In our case for optimization we used the information obtained from PbTe-Ag isopleth.

4. Optimization Procedure

The thermodynamic parameters for all phases in the system were optimized using ThermoCalc software.[14] For this optimization, thermodynamic data for the liquid phase, invariant reactions and phase equilibria were used. To each piece of the selected information a certain weight was given which was based on personal judgment. First, Ag-Te, Pb-Te and Ag-Pb binary systems were optimized, and these optimizations were incorporated into optimization of the ternary Ag-Pb-Te system. The optimization was carried out step by step in agreement with Schmid-Fetzer’s et al.[15] guideline. First, the optimization of the liquid phase was performed, and then the solid phases were assessed. All parameters were finally evaluated together to provide the best description of the system. The calculated interaction parameters are shown in Table 2. For checking of the results of optimization the system was also calculated using Pandat software.[16]

5. Result and Discussion

5.1 Binary Systems

The obtained set of thermodynamic parameters is gathered in Table 2. Calculated phase diagrams of the
### Table 2: Gibbs energies and interaction parameters of Ag-Pb-Te system

| Phase or component | Parameter | $T$, K |
|--------------------|-----------|--------|
| **Liquid**         | $G^\text{Liquid}_{\text{AgTe}} = -19003.825 - 46.68198 \times T + \text{GHSERTE} + 2 \times \text{GHSPB} + \text{GHSERTE}$ | $298.15 < T < 2000.00$ |
|                    | $G^\text{Liquid}_{\text{PbTe}} = -33257.3816 - 23.9402592 \times T + \text{GHSERPB} + \text{GHSERTE}$ |               |
|                    | $G^\text{Liquid}_{\text{AgPb}} = +12902.2744 - 6.60968126 \times T$ |               |
|                    | $G^\text{Liquid}_{\text{AgPbTe}} = -4008.0879 + 1.78184392 \times T$ |               |
|                    | $G^\text{Liquid}_{\text{AgPbTe}} = -2576.13927$ |               |
|                    | $G^\text{Liquid}_{\text{AgPbTe}} = +1791.6784 - 4.6720604 \times T$ |               |
|                    | $G^\text{Liquid}_{\text{AgPbTe}} = 0$ |               |
|                    | $G^\text{Liquid}_{\text{AgPbTe}} = 20000$ |               |
|                    | $G^\text{Liquid}_{\text{AgPbTe}} = -3000$ |               |
|                    | $G^\text{Liquid}_{\text{AgPbTe}} = -12000$ |               |
|                    | $G^\text{Liquid}_{\text{AgPbTe}} = -3000$ |               |
|                    | $G^\text{Liquid}_{\text{AgPbTe}} = +17486.0829 - 10.8584755 \times T$ |               |
|                    | $G^\text{Liquid}_{\text{AgPbTe}} = 2964.38138$ |               |
|                    | $G^\text{Liquid}_{\text{AgPbTe}} = -11491.366 + 9.67716633 \times T$ |               |
| **Ag$_2$Te**       | $G^\text{AG2Te}_{\text{AgTe}} = -10128.93 - 12.645115 \times T + 0.667 \times \text{GHSERAT}$ | $298.15 < T < 2000.00$ |
|                    | $G^\text{AG2Te}_{\text{AgTe}} = +0.333 \times \text{GHSERAT}$ |               |
|                    | $G^\text{AG2Te}_{\text{PbTe}} = 2000 + 0.667 \times \text{GHSERPB} + 0.333 \times \text{GHSERTE}$ |               |
|                    | $G^\text{AG2Te}_{\text{AgPbTe}} = -15000$ |               |
| **Ag$_3$Te$_3$**   | $G^\text{AG3Te3}_{\text{AgTe}} = -11516.052 - 9.0707833 \times T + 0.62 \times \text{GHSERAT}$ | $298.15 < T < 2000.00$ |
|                    | $G^\text{AG3Te3}_{\text{AgTe}} = +0.38 \times \text{GHSERAT}$ |               |
| **Ag$_{65}$Te$_{34}$** | $G^\text{AG65Te34}_{\text{AG2Te}} = -10429.085 - 11.872022 \times T + 0.655 \times \text{GHSERAT}$ | $298.15 < T < 2000.00$ |
|                    | $G^\text{AG65Te34}_{\text{AgTe}} = +0.345 \times \text{GHSERAT}$ |               |
| **PbTe**           | $G^\text{PbTe}_{\text{FCC_A1}} = -76063.2138 + 9.67716633 \times T + \text{GHSERPB} + \text{GHSERTE}$ | $298.15 < T < 2000.00$ |
|                    | $G^\text{PbTe}_{\text{FCC_A1}} = +27610.0621 - 3.68528128 \times T$ |               |
|                    | $G^\text{PbTe}_{\text{FCC_A1}} = -2197.271$ |               |
| **Pb**             | $G^\text{Pb}_{\text{FCC_A1}} = -7650.085 + 101.700244 \times T - 24.5242231 \times T \times \text{LN}(T)$ | $298.15 < T < 600.61$ |
|                    | $G^\text{Pb}_{\text{FCC_A1}} = -0.00365895 \times T \times s^2 - 2.4395E - 07 \times T \times s^3$ |               |
|                    | $G^\text{Pb}_{\text{FCC_A1}} = -10531.095 + 154.234182 \times T - 32.4913959 \times T \times \text{LN}(T)$ | $600.61 < T < 1200.00$ |
|                    | $G^\text{Pb}_{\text{FCC_A1}} = +0.00154613 \times T \times s^2 + 8.05448E + 25 \times T \times s^{-1}$ |               |
|                    | $G^\text{Pb}_{\text{Pb}} = +4157.616 + 53.139072 \times T - 18.9640637 \times T \times \text{LN}(T)$ | $1200.00 < T < 2100.00$ |
|                    | $G^\text{Pb}_{\text{Pb}} = -0.002882943 \times T \times s^2 + 9.8144E - 08 \times T \times s^3 - 2696755 \times T \times s^{-1}$ |               |
|                    | $G^\text{Pb}_{\text{Pb}} = +8.05448E + 25 \times T \times s^{-1}$ |               |
|                    | $G^\text{Pb}_{\text{Pb}} = -2977.961 + 93.949561 \times T - 24.5242231 \times T \times \text{LN}(T)$ | $298.15 < T < 600.61$ |
|                    | $G^\text{Pb}_{\text{Pb}} = -0.00365895 \times T \times s^2 - 2.4395E - 07 \times T \times s^3 - 6.019E - 19 \times T \times s^7$ |               |
|                    | $G^\text{Pb}_{\text{Pb}} = -5677.958 + 146.176046 \times T - 32.4913959 \times T \times \text{LN}(T)$ | $600.61 < T < 1200.00$ |
|                    | $G^\text{Pb}_{\text{Pb}} = +0.00154613 \times T \times s^2$ |               |
|                    | $G^\text{Pb}_{\text{Pb}} = +9010.753 + 45.071937 \times T - 18.9640637 \times T \times \text{LN}(T)$ | $1200.00 < T < 2100.00$ |
|                    | $G^\text{Pb}_{\text{Pb}} = -0.002882943 \times T \times s^2 + 9.8144E - 08 \times T \times s^3 - 2696755 \times T \times s^{-1}$ |               |
| **Te**             | $G^\text{Te}_{\text{Hexagonal_A8}} = -10544.679 + 183.372894 \times T - 35.6687 \times T \times \text{LN}(T)$ | $298.15 < T < 722.66$ |
|                    | $G^\text{Te}_{\text{Hexagonal_A8}} = +0.15183435 \times T \times s^2 - 5.240417E - 06 \times T \times s^3 + 155015 \times T \times s^{-1}$ |               |
|                    | $G^\text{Te}_{\text{Te}} = +9160.595 - 129.265373 \times T + 13.004 \times T \times \text{LN}(T)$ | $722.66 < T < 1150.00$ |
|                    | $G^\text{Te}_{\text{Te}} = -0.0362361 \times T \times s^2 + 5.006367E - 06 \times T \times s^3 - 1286810 \times T \times s^{-1}$ |               |
|                    | $G^\text{Te}_{\text{Te}} = -12781.349 + 147.901226 \times T - 32.5596 \times T \times \text{LN}(T)$ | $1150.00 < T < 1600.00$ |
Section I: Basic and Applied Research

Table 2 Continued

| Phase or component | Parameter | T, K |
|--------------------|-----------|------|
|                    | $G_{\text{Ag}}^\text{Liquid} = -17554.731 + 685.877639 \times T - 126.318 \times T \times \text{LN}(T)$ | 298.15 < T < 626.49 |
|                    | $+ 0.2219435 \times T \times s^2 - 9.42075E-05 \times T \times s^3 + 827930 \times T \times s(-1)$ |      |
|                    | $G_{\text{Ag}}^\text{Liquid} = -3165763.48 + 46756.357 \times T - 7196.41 \times T \times \text{LN}(T)$ | 626.49 < T < 722.66 |
|                    | $+ 7.09775 \times T \times s^2 - 0.00130692833 \times T \times s^3 + 2.58051E+08 \times T \times s(-1)$ |      |
|                    | $G_{\text{Ag}}^\text{Liquid} = +180326.959 - 1500.57909 \times T + 202.743 \times T \times \text{LN}(T)$ | 722.66 < T < 1150.00 |
|                    | $- 0.142016 \times T \times s^2 + 1.6129733E-05 \times T \times s^3 - 24238450 \times T \times s(-1)$ |      |
| Ag                 | $G_{\text{Ag}}^{\text{FCC-AI}} = -7209.512 + 118.202013 \times T - 23.8463314 \times T \times \text{LN}(T)$ | 298.15 < T < 1234.93 |
|                    | $- 0.001790585 \times T \times s^2 - 3.98587E-07 \times T \times s^3 - 12011 \times T \times s(-1)$ |      |
|                    | $G_{\text{Ag}}^{\text{FCC-AI}} = -15095.252 + 190.266404 \times T - 33.472 \times T \times \text{LN}(T)$ | 1234.93 < T < 3000.00 |
|                    | $+ 1.1417733E + 29 \times T \times s(-9)$ |      |
|                    | $G_{\text{Ag}}^{\text{Liquid}} = +3815.564 + 109.310993 \times T - 23.8463314 \times T \times \text{LN}(T)$ | 298.15 < T < 1234.93 |
|                    | $- 0.001790585 \times T \times s^2 - 3.98587E-07 \times T \times s^3 - 12011 \times T \times s(-1)$ |      |
|                    | $- 1.033905E - 20 \times T \times s^7$ |      |
|                    | $G_{\text{Ag}}^{\text{Liquid}} = -3587.111 + 180.964656 \times T - 33.472 \times T \times \text{LN}(T)$ | 1234.93 < T < 3000.00 |

Fig. 1 Calculated Ag-Te binary system

Fig. 2 Calculated Pb-Te binary system

binary Ag-Te, Pb-Te and Ag-Pb systems, compared with experimental data obtained by Kracek et al.,[17] Pelabon,[18] Chikashite and Saito,[19] Wobst,[20] Fay and Gillson,[21] Moniri and Pelot,[22] Gravemann and Wallbaum,[23] Kharif et al.,[24] Kimura,[25] Friedrich,[26] Preckshot[27] and Kleppa[28] are shown in Fig. 1, 2 and 3, respectively. As can be seen from these figures good agreement between the results of calculations and experimental data was found. The Ag-Te binary diagram has been simplified in this work. Instead of allotropic forms of the Ag$_2$Te, Ag$_5$Te$_3$, Ag$_{655}$Te$_{345}$, only one form for each phase was accepted. Following figures show calculated thermodynamic function for the liquid phase in the binary systems. Figure 4 shows the calculated activity of Te in Ag-Te system at 1289 K superimposed with thermodynamic data obtained by Predel and Piehl.[29] Next Fig. 5 shows calculated enthalpy of mixing of liquid Ag-Te phase together with the experimental results obtained by Castanet et al.,[30] Castanet and Bergman,[31] Castanet and Lafitte,[32] Maekawa and Yokokawa,[33] Predel and Piehl.[29] Looking at the comparison of thermodynamic functions with the experimental data as well as the phase diagram one can say...
that associated solution model can be used for thermodynamic modeling of the Ag-Te binary system. Of course, the ionic solution model would be more suitable for tellurium liquid alloys; however, the thermodynamic description will be much more complicated during attempts to describe the ternary system. Calculated enthalpy of mixing of liquid Pb-Te alloys and the chemical potential of Pb in liquid Pb-Te alloy are shown in Fig. 6 and 7 respectively, together with experimental results obtained by Blachnik and Gather,[34] Moniri and Petot,[22] Castanet et al.,[35] Maekawa,[36] Predel et al.,[37] Brebrick and Strauss.[38] The comparison also shows very good agreement with experimental information found in the literature. The last binary Ag-Pb system is an eutectic one. Calculated enthalpy of mixing of the liquid phase, and activity of Pb, are shown in Fig. 8 and 9 respectively. They are compared with the experimental results obtained by Jacob and Jeffes,[39] Castanet et al.,[40] Itagaki and Yazawa,[41] and Hager and Wilkomirsky.[42] Both functions reproduced experimental data very well. It should be mentioned however, that the experimental enthalpy of mixing data show differences between results obtained at similar temperatures.

5.2 Ternary System

Since the binary systems show in general very good agreement between the results of calculations and the experimental data, then it’s possible to calculate the ternary system using Muggianu interpolation. In the case of Ag-Pb-Te system it was necessary to optimize some ternary
parameters. The results are shown in the following Fig. 10, 11, 12, 13. The first one, Fig. 10, shows isopleth Ag₂Te-PbTe superimposed with DTA data obtained by Blachnik and Gather. It is clear from this picture that calculated phase equilibria agree well with the experimental data. In turn, Fig. 11 shows the isopleth PbTe-Ag. Again, this isopleth reproduced experimental information given in Ref 13 well. As it was mentioned before, the third available isopleth Ag₂Te-Pb does not agree with other experimental data. That isopleth was not used during optimization process and is not shown in this work. Calculated at 1173 K enthalpies of mixing for two sections Te-Ag₀₅Pb₀₅ and Te-Ag₀₄Pb₀₆ are shown in Fig. 12 and 13 respectively. A difference between calculated function and the experimental data is less than 1000 J. In this case we can say that enthalpy of mixing of the ternary Ag-Pb-Te system is reproduced well by our parameters. Figure 14 shows calculated isothermal section at 900 K.

5.3 Tellurium Vapor Pressure

Thermodynamic modeling of the ternary Ag-Pb-Te system allows for calculation of tellurium pressure over liquid melts and discussion of lead influence on the tellurium pressure. Gaseous phase of tellurium may contain Te, Te₂, Te₃, Te₄, Te₅ and Te₇ species; however, the dominant molecule is Te₂. The total vapor pressure over liquid tellurium has been determined by Machol and Westrum who described it by the following equation:

\[
\log_{10}(P) = \frac{-10663.15}{T} + 64.7314 - 18.61687 \log_{10}(T) + 0.00341783T
\]

(Eq 5)

where \( P \) is total pressure of Te over the liquid (pressure given in mmHg) and \( T \) is temperature in Kelvin.

Using our model of the liquid phase and Machol and Westrum’s description of tellurium total pressure, the pressure of tellurium over Ag-Pb-Te liquid alloy was calculated. Result of this calculation is shown in Fig. 15. One can see that pressure of tellurium slightly increases when content of lead in the liquid phase increases up to mole fraction of tellurium smaller than 0.25. However, taking into account the difference between absolute

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**Fig. 7** Calculated chemical potential of Te in liquid Pb-Te alloy at 1200 K

**Fig. 8** Calculated enthalpy of mixing of liquid Ag-Pb system at 1200 K

**Fig. 9** Calculated activity of Pb in Ag-Pb binary system
values of pressures for different amount of Pb in liquid, one can say that those differences are negligible up to 0.15 mole fraction of Te. The significant differences appear between 0.15 and 0.2 mole fraction of Te in the liquid phase. The difference cannot be neglected for liquid alloys containing more than 0.2 mole fraction of Te. For this tellurium content and $X_{Pb} > 0.3$, the addition of lead increases pressure of tellurium significantly. It can be explained by smaller interaction between Ag and Te when Pb is added. In other words, the activity of Te in the liquid

Fig. 10  Isoplethal section Ag$_2$Te-PbTe superimposed with Blachnik and Gather result

Fig. 11  Isoplethal section PbTe-Ag compared with Romerman and Blachnik results
phase becomes less negative when Pb is added and because of that the pressure of Te increases, in agreement with Raoult’s law.

6. Conclusions

The thermodynamic modeling of the ternary Ag-Pb-Te system was performed based on the literature information and a set of thermodynamic parameters was obtained which were then used to reproduce known data. Good agreement between calculations and experimental results was found. With the obtained thermodynamic description of the liquid phase, lead influence on tellurium pressure over Ag-Pb-Te alloys was shown that an increase in lead content of an alloy increases the vapor pressure of tellurium.

Acknowledgments

The authors are grateful to Narodowe Centrum Badań i Rozwoju for financial support under grant no. 0364/R/T02/2008/04 and to National Taiwan Science Council for financial support under Grant no. NSC-98-2218-E-155-005.
