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Effect of oxygen on trace impurities in extremely pure metal ingots used for realising ITS-90 fixed point temperatures

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Effect of oxygen on trace impurities in extremely pure metal ingots used for realising ITS-90 fixed point temperatures

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Abstract. The International Temperature Scale of 1990 (ITS-90) provides a scheme for calibrating thermometers which is largely based on the freezing points of pure metals such as indium, tin, zinc, aluminium and silver. The existence of trace impurities in pure metals results in uncertainties in the realization of these freezing points. Several methods such as the sum of individual estimates (SIE) and overall maximum estimate (OME) are used to assess the uncertainties due to the presence of impurities. However, it is becoming evident that the oxidation of impurities results in their precipitation, which means that these insoluble oxides no longer play a significant role in the elevation or depression of the freezing temperature. Hence the conventional correction techniques may overestimate the magnitude of the effect. In this study, the thermodynamic modelling software MTDATA was used to evaluate the effect of oxygen on selected impurities in In, Sn, Zn, Al and Ag by calculating the binary impurity-metal phase diagram in the presence of specific amounts of oxygen. It was found that oxygen has a significant effect on many of the systems studied. The most significant effect was observed in the Ag system, and then, in decreasing order of significance, In, Sn, Zn and Al.

1. Introduction

Impurities present at the level of parts per million (ppm) in very pure metal ingots results in an elevation or depression of the freezing temperature [1]. The impurity also adds to the error in the calibration of a standard platinum resistance thermometer (SPRT) [2]. Impurities in pure metal substances are a major source of uncertainty in realising the International Temperature Scale of 1990 (ITS-90) [3] fixed-point temperatures [2]. There are several techniques for accounting for the influence of impurities [4,5] and these have recently been compared using an aluminium fixed point [6]. A key technique for quantifying the effect of given impurities is the Sum of Individual Estimates (SIE) method [4,5,7,8]. This relies on a knowledge of the amount of each impurity present x_i and the corresponding liquidus slope dT/dx_i. The overall depression or elevation of the freezing temperature is then given by:

$$\Delta T = \sum x_i \frac{\partial T}{\partial x_i} \quad (1)$$

The SIE method is recommended by the Consultative Committee for Thermometry to correct the effect of impurities on the realisation of fixed points [4]. Recently, great progress has been made in characterising the

liquidus slopes for a wide range of binary alloys relevant to ITS-90 fixed points [1,9]. However, two distinct challenges remain: the first is the accuracy and traceability of sufficiently sensitive chemical assays capable of detecting the very small concentration of impurities; and the second is the limited knowledge of the effect of impurity oxides formed [4]. This question has recently come to the fore with direct experimental measurements of the effect of oxide formation on the melting and freezing curves [10]. This work addresses the latter point, by performing thermodynamic calculations to evaluate the influence of oxygen on the binary alloy phase diagrams of a number of typical binary alloy systems found in ITS-90 fixed points.

2. Method

The phase diagrams of solvent-solute-oxygen systems were calculated using the thermodynamic modelling software MTDATA version 6.0. MTDATA can calculate equilibria using true Gibbs energy minimisation [11] of a system with respect to the proportions of individual species that could form. This software can calculate the equilibrium state at a fixed temperature and pressure. The most stable state has the lowest Gibbs free energy [9].

Selective oxidation can be helpful in removing dissolved impurities from pure metals and negating their influence on the freezing temperature. A possible source of oxygen in a fixed-point cell is the impure argon atmosphere in the cell [12]. Certain impurities have a higher propensity to react with oxygen than others. Oxides that are formed will generally precipitate out of the solution and will have no further effect on the freezing temperature. The formation of oxides will reduce the amount of oxygen available, and once the oxygen is used up the remaining impurities, even if susceptible to oxidation, cannot be oxidised. It is therefore of interest to know how the binary (impurity-metal) phase diagram looks for a given ‘starting’ amount of oxygen. Two further points are that the oxides of noble elements (present or added to fixed-point metal) will reduce to elemental form, and elements which are highly reactive with oxygen will always precipitate as an oxide [13].

The databases used in MTDATA in the following order of priority for the In, Al, Sn and Zn systems was SGSOL, SOLDERS, SILVER, MTOX, MTOXSUP, MTAL, MTSOLDERS [5]. For the Ag system the databases used were SILVER, MTOX, MTOXSUP, SGSOL, SOLDERS, MTAL, and MTSOLDERS. Chemical ordering phases were ignored in the calculations.

MTDATA version 6.0 was used to generate solvent – solute – oxygen phase diagrams where the amount of oxygen was varied in 20 ppm steps from 100 ppm down to 20 ppm. The total concentration of oxygen was kept fixed for the generation of the phase diagram, mostly at either 100 ppmw or 1000 ppmw.

3. Results and discussion

The data acquired for the aluminium and indium systems were found to be in general agreement with prior (preliminary) MTDATA calculations [1].

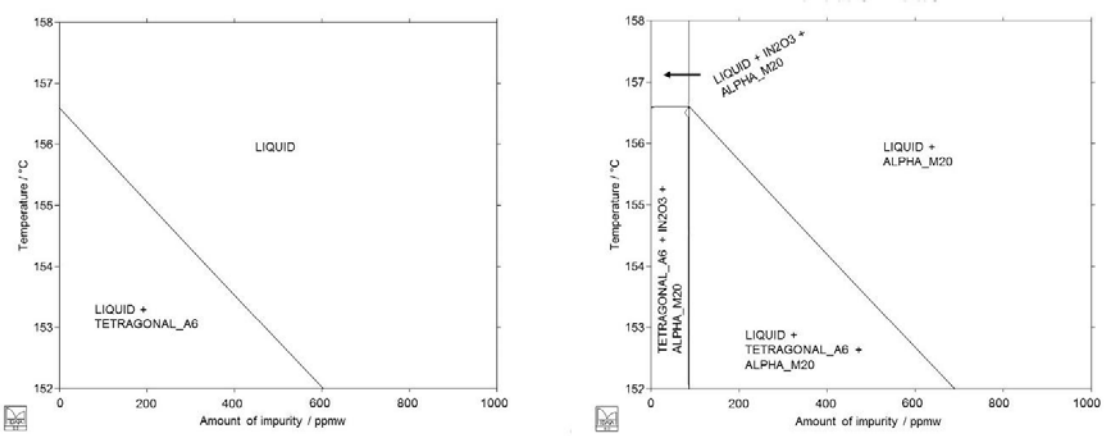


Figure 1. Phase diagrams of the In-Li system (Li is the impurity). Left: In-Li system when there is no oxygen present. Right: In-Li-O; there is 100 ppm of oxygen present, which is clearly suppressing the effect of the Li impurities on the freezing temperature of In. Once all the oxygen is used up (this requires about 80 ppmw Li), the liquidus slope assumes the same value as when no oxygen is present.

The phase diagrams in Figure 1 show the effect of oxygen on the In-Li system, where the oxygen clearly inhibits the effect of impurity Li (solute) on the fixed-point metal (solvent). This is due to the formation of insoluble oxides [12,13]. Once the compounds are formed, they have no effect on the freezing temperature of the fixed-point metal. This means that the freezing temperature stays at a constant value [1] corresponding to that of the pure solvent. As more impurity is added to the system, the formation of compounds continues until the oxygen is used up. At this 'threshold impurity' concentration, there is no longer any oxygen available to form compounds, and the addition of further impurity results in a depression of the freezing point. In the In-Li system, this results in the appearance of a negative liquidus slope, with the expected value (i.e. the same value as that in the oxygen-free system), at the threshold impurity concentration in Figure 1.

This threshold impurity concentration of In-Li-O system is displayed in Figure 2 as a function of the amount of oxygen present in the system. The threshold impurity concentration starts from 17.2 ppm and then steadily increases. The threshold impurity concentration is proportional to the amount of oxygen present. Table 1 presents the threshold impurity concentration corresponding to different amounts of oxygen for all the systems studied.

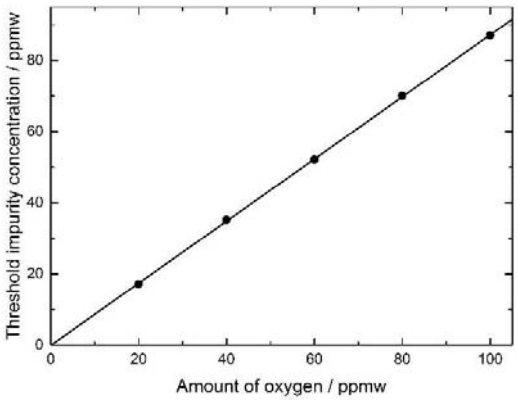


Figure 2. Graph showing the relationship between the threshold impurity concentration and the amount of oxygen present in the system In-Li-O. Line represents best fit curve.

Table 1. Tabulated values of the threshold impurity concentration for each fixed point metal as well as the corresponding value of the liquidus slope. Asterisk denotes absence of oxides in the phase diagram.

Fixed point	Impurity	Proton number	Liquidus slope / mK ppmw^{-1}	*Amount of oxygen (ppmw):*	Threshold impurity concentration (ppmw)					
					100	*80*	*60*	*40*	*20*	*10*
In	Li	3	0.87		87.0	70.1	52.1	35.2	17.2	
	Na	11	2.88		289.0	231.4	172.5	114.9	58.9	
	Mg	12	1.51		152.9	121.4	91.3	61.1	31.8	
	Al	13	1.13		113.6	90.0	67.9	45.3	22.8	
	Ca	20	2.49		251.0	201.3	151.5	101.8	52.1	
	Ti	22	4.47		447.4	359.7	269.3	180.3	90.0	
	V	23	2.12		213.1	169.9	128.0	86.1	42.9	
	Cr	24	2.17		218.8	176.0	130.9	90.4	44.2	
	Sr	38	5.45		545.3	438.4	325.7	219.9	109.5	
	Zr	40	2.85		285.1	228.8	172.5	113.6	57.3	
	Nb	41	5.8		581.4	464.4	349.2	232.7	117.4	
	Ba	56	8.57		858.4	688.2	516.7	345.3	172.5	
	La	57	5.81		580.9	464.4	347.9	232.7	116.2	
	U	92	7.46		745.8	596.6	447.4	298.1	148.9	
Sn	Li	3	0.87		86.9	69.5	52.1	34.7	17.3	8.6
	B	5	0.45		45.4	36.2	27.3	18.2	9.0	
	Na	11	1.45		144.4	115.2	87.4	57.5	28.8	
	Mg	12	1.52		152.9	121.9	91.5	61.1	31.8	
	Al	13	1.12		111.9	89.4	67.2	44.7	22.4	
	P	15	0.78		77.6	62.0	46.5	31.0	15.6	
	K	19	1.62		163.3	130.6	97.9	66.5		
	Ca	20	2.5		251.0		151.5		50.8	
	Ti	22	2		200.0	160.7	118.8	79.6	40.3	
	Cr	24	2.18							
	Sr	38	5.48		548.1	439.5	329.6		109.7	
	Zr	40	2.85		285.1	230.1	172.5	114.9	57.3	
	Ba	56	8.58		859.7	688.2	515.4	344.0	173.8	
	La	57	5.79		579.6	463.1	347.9	231.4	116.2	
	U	92	7.46		745.8	596.0	446.2	298.7	148.9	
Zn	Li	3	0.87		86.9	69.5	52.2	34.8	17.4	
	B	5	0.45		45.1	36.0	27.1	18.0	9.0	
	Mg	12	1.51		152.9	124.1	92.6	62.5	32.4	
	Al	13	1.13		113.6	90.0	67.8	45.5	23.3	
	Si	14	0.88		88.7	71.7	53.4	35.1	19.3	
	Ca	20	2.51		252.3	201.3	151.5	101.8	50.8	
	Ti	22	2.01		200.0	160.7	120.1	80.0	39.8	
	V	23	2.13		214.4	171.2	128.0	86.1	44.2	
	Cr	24	1.63		165.9	131.9	99.2	67.8	35.1	
	Ba	56	8.58		859.7	688.2	516.7	344.0	173.8	
	La	57	5.80		580.2	463.1	349.2	231.4	116.2	
	U	92	7.43		744.5	596.6	446.0	299.5	150.2	
Al	Li	3	0.05		6.3	5.5	4.4	3.4	2.2	
	Sr	38	0.29		29.2	23.8	17.8	11.9	6.0	
	Ba	56	0.46		45.5	36.1	27.1	18.0	9.0	
Ag	Li	3	0.88		88.7	70.4	53.2	35.2	17.5	9.3
	B	5	0.45		56.0	48.1	39.0	32.4	20.6	15.0
	Mg	12	1.53		152.9	124.1	92.6	61.2	31.1	15.8
	Al	13	1.13		112.3	90.4	67.4	44.9	22.4	11.2
	Si	14	0.88		87.4	70.1	51.9	34.9	17.0	8.0
	P	15	0.77		76.9	61.5	46.3	30.3	15.3	7.4
	Ca	20	2.5		250.3	200.7	150.1	100.5	50.6	25.5
	Ti	22	1.5		151.2	121.4	91.5	60.0	31.6	16.3
	V	23	2.12		211.8	169.9	127.5	84.8	42.4	21.3
	Cr*	24	2.03		213.1	172.5	131.9	91.3	50.8	
	Fe*	26	2.38		237.9	186.9	139.8	94.0	46.8	
	Co*	27	3.57		364.9	289.0	220.9	148.9	78.2	
	Ni*	28	3.66		372.7	300.8	252.3	160.7	76.9	
	Zn*	30	4.03		409.4	321.7	248.4	167.3	83.6	
	As*	33	3.15		312.3	251.0	190.8	121.4	62.5	
	Sr	38	5.46		548.1	440.8	333.5	219.6	112.3	
	Zr	40	2.89		287.7	231.4	169.9	113.6	56.7	28.2
	In*	49	4.84		498.4	404.2	312.5	213.1	109.7	
	Sb*	51	5.05		502.3	401.5	300.8	201.3	96.6	49.5
	Ba	56	8.55		858.4	686.9	514.1	344.0	171.2	91.3
	Bi*	83	8.49		844.0	642.4	491.9	347.9	141.1	70.4
	La	57	5.75		578.2	461.8	346.6	231.4	121.4	57.3
	U	92	7.47		743.2	591.3	446.0	297.2	142.4	71.7

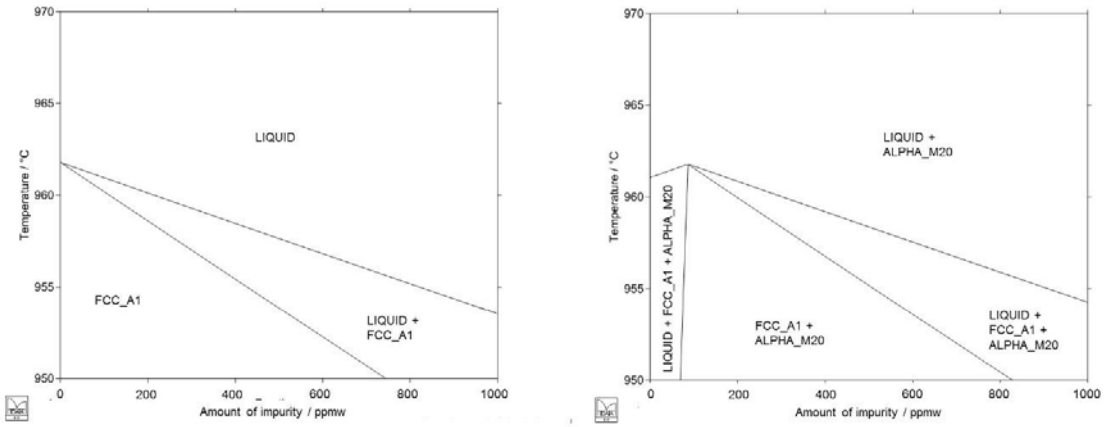


Figure 3. Phase diagrams of the Ag-Li system (Li is the impurity). Left: Ag-Li system when there is no oxygen present. Right: Ag-Li-O; there is 100 ppm of oxygen present, there is a clear non-zero liquidus slope that tends to the normal freezing temperature value as the amount of oxygen present is decreasing.

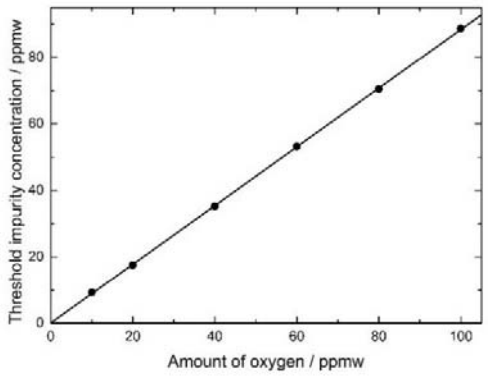


Figure 4. Graph showing the relationship between the threshold impurity concentration and the amount of oxygen present in system Ag-Li-O.

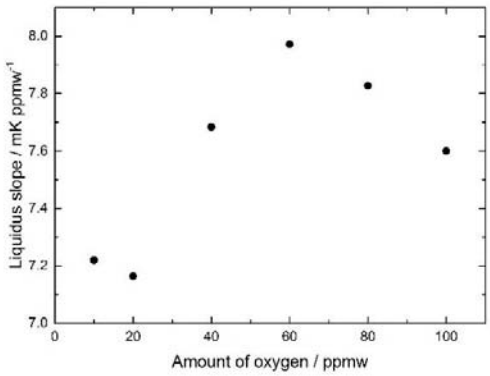


Figure 5. Graph showing the relationship between the liquidus slope and the amount of oxygen present in system Ag-Li-O.

The case for the silver fixed point is more complicated than for the other systems, because of the strong effect of dissolved oxygen on the freezing temperature of silver [13]. The phase diagrams in Figure 3 show the effect of oxygen on the Ag-Li system where there is a formation of oxides that precipitate out. In contrast to Figure 1, the liquidus slope is not constant at the pure freezing temperature value of silver in the limit of low impurity concentration. Instead the temperature starts at a lower value and increases to the pure value at the threshold impurity concentration (i.e. where the dissolved oxygen concentration reaches zero and the oxides have no effect on the freezing temperature). From the threshold, the freezing temperature then decreases again in correspondence with the normal behaviour in the absence of oxygen (exhibited in the Ag-Li system on the right). The dependence of the threshold impurity concentration on oxygen content shown in Figure 2 exhibits the same behaviour shown in Figure 4. The threshold impurity concentration is also shown to be proportional to the amount of oxygen present for the Ag-Li-O system. This appears to be a general trend across all the systems examined. The liquidus slope at impurity concentrations below the threshold exhibits a slight variation

with oxygen concentration; this is shown in Table 2 and is plotted as a function of the amount of oxygen present (Figure 5). It is thought that this variation is due to the numerical accuracy available from MTDATA at these extremely low impurity concentrations. Figure 5 shows that the liquidus slope versus the amount of oxygen present in the system can be approximated to be constant. There are slight variations but overall the trend shows that, in general, the liquidus slope doesn't change dramatically when there is varying amounts of oxygen present.

Table 2. The calculated liquidus slope of Ag systems (before the threshold impurity concentration) (units of mK $ppmw^{-1}$) tabulated for differing amounts of oxygen present. Asterisk denotes absence of oxides in the phase diagram.

Impurity	Amount of oxygen present / ppmw					
	100	80	60	40	20	10
Li	7.6	7.8	8.0	7.7	7.2	7.2
B	56.0	48.1	39.0	32.4	20.6	15.0
C*						
N*						
O						
Na						
Mg	152.9	124.1	92.6	61.2	31.1	15.8
Al	112.3	90.4	67.4	44.9	22.4	11.2
Si	87.4	70.1	51.9	34.9	17.0	8.0
P	76.9	61.5	46.3	30.3	15.3	7.4
S*						
K						
Ca	250.3	200.7	150.1	100.5	50.6	25.5
Ti	151.2	121.4	91.5	60.0	31.6	16.3
V	211.8	169.9	127.5	84.8	42.4	21.3
Cr*	213.1	172.5	131.9	91.3	50.8	
Mn*						
Fe*	237.9	186.9	139.8	94.0	46.8	
Co*	364.9	289.0	220.9	148.9	78.2	
Ni*	372.7	300.8	252.3	160.7	76.9	
Cu						
Zn*	409.4	321.7	248.4	167.3	83.6	
As*	312.3	251.0	190.8	121.4	62.5	
Se*						
Sr	548.1	440.8	333.5	219.6	112.3	
Zr	287.7	231.4	169.9	113.6	56.7	28.2
Nb						
Ag						
Cd*						
In*	498.4	404.2	312.5	213.1	109.7	
Sn						
Sb*	502.3	401.5	300.8	201.3	96.6	49.5
Te*						
Ba	858.4	686.9	514.1	344.0	171.2	91.3
Pb*						
Bi*	844.0	642.4	491.9	347.9	141.1	70.4
La	578.2	461.8	346.6	231.4	121.4	57.3
U	743.2	591.3	446.0	297.2	142.4	71.7

Table 3. Representation of the possibility of oxidation of impurities in the fixed point metals; components of the periodic table are the impurities present. Note: Left column represents the current MTDATA calculations (red: liquidus slope is zero up to a threshold impurity concentration; amber: liquidus slope is zero at all impurity concentrations; yellow: oxygen affects the phase diagram but the liquidus slope takes the same value as in the absence of oxygen (non-zero); green: oxygen has no effect; blue: oxides are present but slope is zero even in the absence of oxygen; light green: oxygen affects the phase diagram and the slope is zero; pink (only for silver):

liquidus slope value is non-zero up to an impurity threshold concentration; asterisk (only for silver) denotes that the system has no oxides present; purple (only for silver): complex system that requires more research. The centre column represents previous MTDATA calculations of Pearce et al [1]. The right column shows the findings of Fahr and Rudtsch [12] (red: oxidation likely; amber: oxidation probable; green: oxidation unlikely).

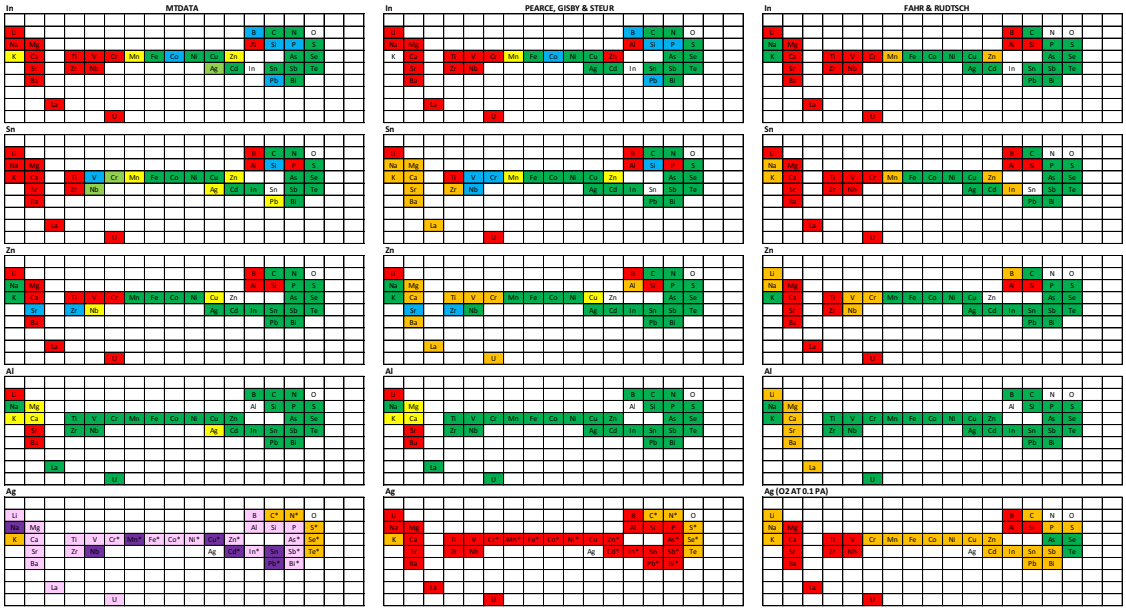


Table 4. The calculated percentages for each system (oxygen and the fixed-point metal of the system in question was not included).

Fixed point metal	Number of impurities where the liquidus slope changed due to oxygen	Number of impurities where oxygen has effect	Number of systems where oxygen has no effect	Number of systems with no oxides in phase diagram	% of system where liquidus slope changed	% of system where oxygen has effect	% of system where oxygen has no effect	% of systems with no oxides in phase diagram
In	14	23	13	0	38.9	63.9	36.1	0.0
Sn	14	22	14	0	38.9	61.1	38.9	0.0
Zn	12	16	20	0	33.3	44.4	55.6	0.0
Al	3	7	29	0	8.3	19.4	80.6	0.0
Ag	23	36	0	18	63.9	100.0	0.0	50.0

The influence of oxygen on the systems examined in this study are summarised in Table 3. The aluminium and indium systems were found to be in agreement with previous findings [1,12]. However some differences were observed for the zinc, tin and silver systems, possibly due to upgrades in the MTDATA databases, or the much larger number of parameter sweeps performed in this study compared with that in [1].

Indium: Table 3 shows that many of the impurities in the In system oxidise and precipitate out of the fixed-point metal. There are some cases where oxygen has no effect on the liquidus slope. Oxygen affects 64% of In systems, and changes the liquidus slope for 39% of systems (Table 4), so the effect of oxygen must be taken into consideration when using In fixed-point cells.

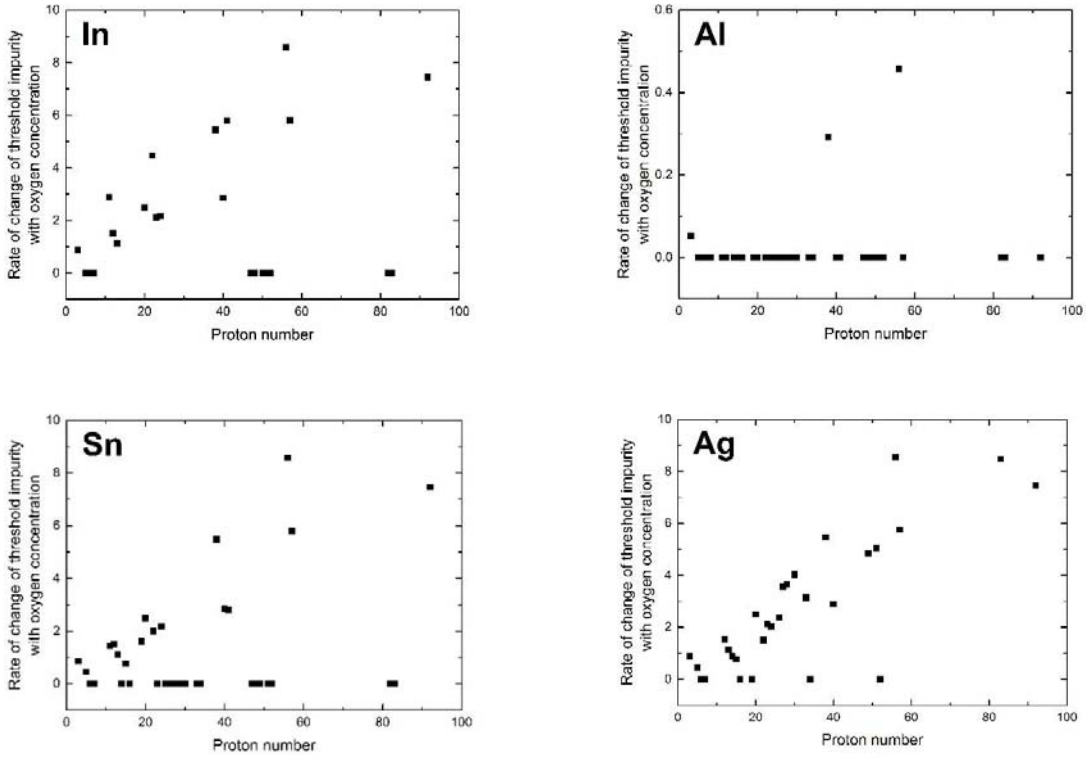
Tin: More impurities oxidise and precipitate out of tin fixed-point cells than zinc and aluminium cells. Oxygen affects roughly 61% of Sn systems. Also for 39% of Sn systems, oxygen alters the liquidus slope (Table 4). Like the Zn system, oxygen affects the liquidus slopes in Sn-Li and Sn-U phase diagrams.

Zinc: 12 impurities in the Zn system oxidise and precipitate out of the fixed-point metal. Figure 6 shows that, where a threshold impurity exists, there is a correlation between the rate of change of the threshold impurity with overall oxygen concentration and the proton number of the trace impurity. Table 3 shows that the majority of impurities studied have no effect on the liquidus slope. Oxygen affects all the alkaline earth metals in Table

3 but the liquidus slope for Sr doesn't change. The ability of oxygen to alter the liquidus slope decreases as the proton number increases for transition metals. B and Si are the only non-metal impurities that form a compound with oxygen. Also Li (lanthanoid) and U (actinoid) form an insoluble compound with oxygen. Oxygen affects about 44% of Zn systems (Table 4).

Aluminium: Many of the impurities in the Al system do not oxidise and precipitate out of the fixed-point metal. There is again a correlation between the rate of change of the threshold impurity with overall oxygen concentration and the proton number of the trace impurity for the Al system, notably for the Li (alkali metal), Sr (alkaline earth metal) and Ba (alkaline earth metal) impurities; also this rate of change is much smaller than for the other systems (Figure 6). This suggest that for the Al system, impurities that are alkali will change the liquidus slope. Oxygen affected only 19% of Al systems (Table 4) which is the lowest rate of all the systems. It seems likely that in an experimental setting the effect of oxygen on Al fixed-point cells needs to be taken into account for only a few impurities.

Silver: Oxygen affects 100% of the Ag systems and 50% of the phase diagrams considered have no oxides present. The Ag system is the only one that had no oxides in some phase diagrams. There were systems (Table 3) that were too complicated to enable a straightforward determination of the threshold impurity concentration. The systems of most interest are the following: Na, Mn*, Cu*, Cd*, Sn, Nb and Pb* (* denotes no oxides were present in the phase diagram). Therefore the effect of oxygen must be considered when using silver fixed-point cells.



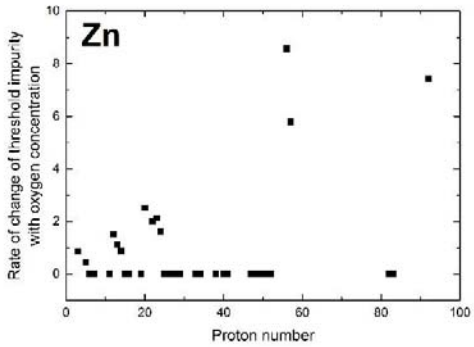


Figure 6. Rate of change of threshold impurity concentration with oxygen concentration, as a function of impurity proton number, for the five systems studied.

4. Conclusion

Thermodynamic calculations of the impurity-metal-oxygen phase diagrams have been performed to evaluate the effect of oxygen on the impurity-metal liquidus line arising from oxidation of impurities and their subsequent precipitation. The calculations show that impurities do, in general, oxidize and precipitate out of solution, with a resulting negation of their effect on the freezing temperature. The amount of impurity oxidised as a function of the amount of oxygen present has been tabulated, which paves the way for eliminating certain impurities from SIE calculations if the amount of oxygen present in the fixed point cell environment is known.

It was found that oxygen has the most effect on the silver fixed point, and the least effect on the aluminum fixed point. Tin and indium systems yield a comparable number of impurities that form compounds with oxygen and exhibit an altered liquidus slope. Overall oxygen does have an effect on fixed-point cells but at differing levels. More research is needed to create a comprehensive database with definitive information on which compounds are formed in the presence of oxygen. However, this is currently beyond the capability of MTDATA, except for the limited number of cases. As the supporting databases grow, the number of systems that can be studied will also be enlarged.

Acknowledgments

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