

THE POSSIBILITY OF RECOVERING INDIUM METAL FROM ACIDIC SOLUTIONS BY CEMENTATION

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Abstract

Indium recycling by a hydrometallurgical method must include the reduction of the dissolved ionic In compound to its metallic state. We have examined the easily implemented cementation of In with Fe, Zn, Mn, Al and Mg. It was found that the cementation with Zn turns slow as the produced layer lacks sufficient porosity to allow the solution to reach the metal surface, and the strongly adhering deposit is hard to be removed. On the other hand, Al may perform efficiently if the pH is set correctly. The indium layer is fast growing, can be easily removed. After mechanical compacting, it is easily melted. The Al consumption is close to the stoichiometric value at pH 1 and the produced indium sponge can be of 99.99% purity.

Keywords: indium; cementation, contact reduction, LCD recycling

1. Introduction

Indium is a critical metal, whose supply shortage may have serious economic impacts on the short run. Primary resources – as minor components of some ores of major non-ferrous metals – are relatively scarce (Choi et al., 2014; Alfantazi and Moskalyk, 2003). The primary production of indium is mostly related to the mining of sphalerite ores and zinc metallurgy (Zhang et al., 2016; Koleini et al., 2010). The currently processed waste materials are mostly the indium-tin-oxide sputtering targets. However other secondary resources – as the liquid crystal display panels – may become increasingly important (Li et al., 2015). Secondary indium production is dominated by hydrometallurgy. While leaching of In is a relatively straightforward technology, sufficiently covered in literature, the recovery of metallic In from the solution has not been treated in similar detail. The processes and the specific conditions of neither the contact nor the electrolytic indium deposition has been reported. Therefore, a fundamental examination of such processes is required if pure In recovery is intended.

2. Thermodynamic study of the processes

Contact reduction, or as it is technically termed, cementation of indium involves the reduction of the hydrated In^{3+} ions in solution by another metal (Me) of valence x :



or by cathode of sufficiently lower potential than that of the electrode potential of the In^{3+}/In couple:

$$\text{In}^{3+} + 3e^- = \text{In}, \quad E_{\text{In}^{3+}/\text{In}} = E_{\text{In}^{3+}/\text{In}}^\ominus + \frac{\mathbf{R}T}{3\mathbf{F}} \ln a_{\text{In}^{3+}} \quad (2)$$

where E is the electrode potential with E^\ominus as its standard value and a is the activity of the indicated ion, T is the thermodynamic temperature, \mathbf{R} is the universal gas constant and \mathbf{F} is the Faraday constant.

The implementation of cathodic reduction is technically more demanding than the contact reduction (cementation), which can be carried out in a simple way by contacting the reagent metal with the indium solution. In both cases the required electrons can be supplied through a flat surface of a metal sheet, allowing a simple physical removal of the deposited indium layer. The desired reduction of In^{3+} ions is theoretically possible by providing a reaction surface with lower potential than that of the In^{3+}/In equilibrium electrode potential.

In contact reduction, ideally a stoichiometric amount of the reagent metal will go into solution, as expressed by Eq (1). There is a concentration gradient developing at the interface, which induces the necessary diffusion transport of the ions, but it adversely affects the thermodynamic conditions of the reaction. As the indium layer is formed, the generated Me^{x+} ions of the reagent metal need to be transported across it. Therefore, the physical structure – with its inherent porosity - is a key factor. In contrast to the physically stable cathode surface, the reagent metal of contact reduction and its impurities may contaminate the product. Thus in this procedure, the choice of the reagent metal and the efficiency of the process is limited.

The choice of the reducing metal can be based on standard Gibbs free energy changes (ΔG^\ominus), seen in Fig. 1a. The largely negative values of the energy changes in the system indicates that cementation with Al and Mg is highly preferred. Also, a significant amount of heat is liberated, as shown in Fig. 1b.

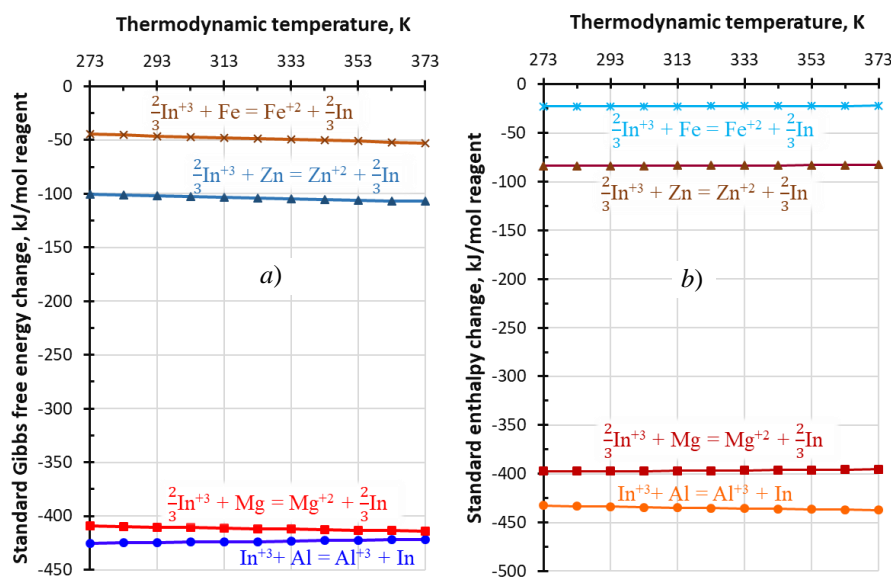


Figure 1. The standard Gibbs free energy change (a) and the standard enthalpy change (b) of In cementation with different reagents.

The reaction may proceed as long as the actual change in the Gibbs free energy (ΔG) is negative:

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{Me}^{x+}}^x}{a_{\text{In}^{3+}}^3} < 0 \quad (3)$$

as expressed generally for the reactions in Fig. 1. The difference in the standard electrode potentials ($E_{\text{In}}^\circ - E_{\text{Me}}^\circ$) and the standard Gibbs free energy change of the corresponding cementation reaction ($\Delta G_{\frac{x}{3}\text{In}^{3+} + \text{Me}}^\circ$) are directly interrelated:

$$\Delta G_{\frac{x}{3}\text{In}^{3+} + \text{Me}}^\circ = -\frac{x}{3} F (E_{\text{In}^{3+}/\text{In}}^\circ - E_{\text{Me}^{x+}/\text{Me}}^\circ) \quad (4)$$

Applying the relationship of the electrode potential and the Gibbs free energy associated with the reduction of metal ions, a more convenient criterion of the cementation process is usually considered:

$$E_{\text{In}}^\circ + \frac{RT}{3F} \ln a_{\text{In}^{3+}} - E_{\text{Me}}^\circ - \frac{RT}{xF} \ln a_{\text{Me}^{x+}} > 0 \quad (5)$$

The relevant standard electrode potentials of In, Fe, Al and Mg are -0.34 V, -0.44 V, -0.76 V, -1.66 V and -2.36 V, respectively (Vanhees et al., 1981).

The temperature dependence of the reactions can be assumed by the Gibbs free energy change – calculated with the HSC Chemistry software – as plotted in Fig 1. It is seen that temperature does not affect appreciably the thermodynamic conditions of the cementation reactions. On the other hand, the kinetic conditions in the aqueous systems are strongly influenced by the temperature. The enthalpy changes of the examined reactions are generally negative, thus the cementation process – especially with aluminium as the reductant – can be strongly exothermic, therefore the temperature may rise during the process. Applying higher temperatures can significantly enhance both the diffusions of the hydrated ions and the charge transfer steps. Stirring is an obvious requirement to assist the transfer of the ions.

The best candidates as reducing agents are metals of significantly lower standard electrode potentials than that of In, resulting in more negative Gibbs free energy changes of the cementation reactions shown in Fig. 1. In such cases the reaction may proceed to virtual completion, as expressed by Eq. (5). The slight difference in the standard redox potentials of the In^{3+}/In and the Fe^{2+}/Fe couples and the correspondingly slightly different standard Gibbs free energies of the reaction indicates a possibly incomplete cementation, strongly influenced by the activities of the ions. As derived from Eq. (5), equilibrium is reached as soon as the activity ratio near the actual reaction surface becomes:

$$\ln \frac{\sqrt[x]{a_{\text{Me}^{x+}}}}{\sqrt[3]{a_{\text{In}^{3+}}}} = \frac{F(E_{\text{In}}^\circ - E_{\text{Me}}^\circ)}{RT} \quad (6)$$

It infers that even with the weakest reductant considered here, i.e. iron, the indium concentration in an originally pure solution of 298 K temperature can be reduced to approximately 10 000 times lower. However, if the solution initially contained 1 g/dm³ iron, the indium concentration can only be reduced ~ 500 times. Therefore, the reducing power of iron immersed in an indium solution is quickly lost as the cementation proceeds. With zinc, however, the equilibrium activity ratio expressed by Eq. (6) is orders of magnitude higher, and with aluminium even higher. Thus there is no obstacle from a thermodynamic point of view in the way of executing the proposed cementation efficiently if Zn or Al is used.

A further practical aspect is the cost of the reagent metal. Aluminium – with its largely negative standard electrode potential - offers excellent thermodynamic properties and it has the added advantage of high ionic charge, which means lower stoichiometric requirement. However, iron in the form of unalloyed steel is evidently the cheapest. Calculated theoretical specific consumptions are marked with empty bars and the approximate material costs are overlaid as solid columns in Fig. 2. Although of lower commercial purity, aluminium seems a good choice, while zinc may not be cost effective.

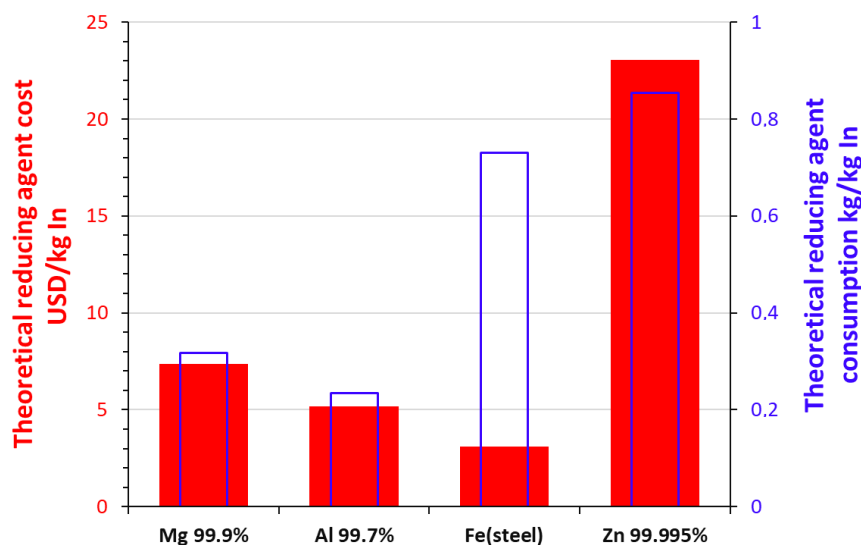


Figure 2. The stoichiometric consumption of the cementing agents and their associated price.

An important aspect is the purity of the deposited In product, which may be adversely affected by the impure common mild steel as the reductant. High grade (99.7%) primary aluminium is still relatively cheap, and could provide a purer In product. Zinc is usually available at higher purity but the specific consumption is also high.

3. Experimental procedure

The pure indium starting solutions from which the cementation was carried out were made by dissolving 99.999% In metal in concentrated HCl, followed by proper dilution to 10 g/dm³ concentration and setting the required pH by controlled addition of NaOH solution from a burette. Each reducing agent was examined under the same initial settings. For a wider scope, more reducing agents were experimentally examined than those characterised by Fig. 2. The experiments included the examination of unalloyed C45 grade steel, 99.995% pure Fe, smelter grade 99.7% Al, 99.9% Mg, electrolytic 99.7% Mn and commercial grade 99.995% Zn. Except for the Mg rod, each reducing metal was used in the form of a thin sheet, as shown in Fig. 3.a and b. Samples were regularly taken – as seen in Fig. 3.c, with micro pipettes. They were diluted and analysed using flame atomic absorption spectrometry (FAAS) illustrated by Fig. 3.d. The potential of the working electrode was measured against a saturated calomel electrode with a digital multimeter. All the experimental runs were intended to approach equilibrium, and thus lasted for at least an hour, while steady stirring at the rate of 350 r.p.m. was applied and samples were taken at regular intervals.



Figure 3. The materials and the process of cementation (a, b), the sampling (c) and the analysis (d).

4. Results and discussion

The first set of experiments were carried out at 55°C and pH 1 in order to see the efficiency of the most practical reducing agents. Results are presented in Fig. 4.

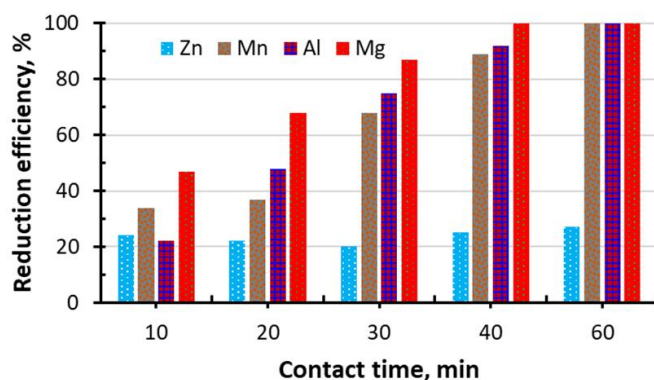


Figure 4. The efficiency of different agents in the cementation of indium (55 °C, pH 1).

Iron is not included in Fig. 4, as it (in the form of unalloyed steel) resulted in no practically recognisable change in the solution composition. The theoretical difference in the electrode potentials wasn't sufficient to reduce In to the metallic state. It can be seen, that Zn is initially active, but later it is passivated as the cemented indium layer adheres tightly to the surface, allowing no solution to pass through. While Mn was effective at reducing In, the produced sponge was not readily removable from the surface, and it is not a common metal product. On the other hand, Al and Mg proved to be excellent cementing agents, both resulting in fast and efficient reduction of In. As expected from the thermodynamic properties, the temperature of the solution was observed to increase by the reaction heat. This effect was especially strong in the case of Mg. It is understandable, as the data of Fig. 1.b is converted to molar enthalpies referring to the amount of reduced indium. With the most active reducing agents, the side reaction of dissolution by the acid becomes intensive. The intensity of hydrogen

evolution also influences the cementation. When Mg was used, so much hydrogen is evolved that even the danger of explosion cannot be excluded. In the case of aluminium as the applied reducing agent, the control of the pH and the temperature can assure a balanced process. The intense agitation caused by this effect also disperses some of the In sponge as fine particles in the solution, decreasing the yield. Figure 5 shows the macro and microphotographs of the cemented In on Zn surface.

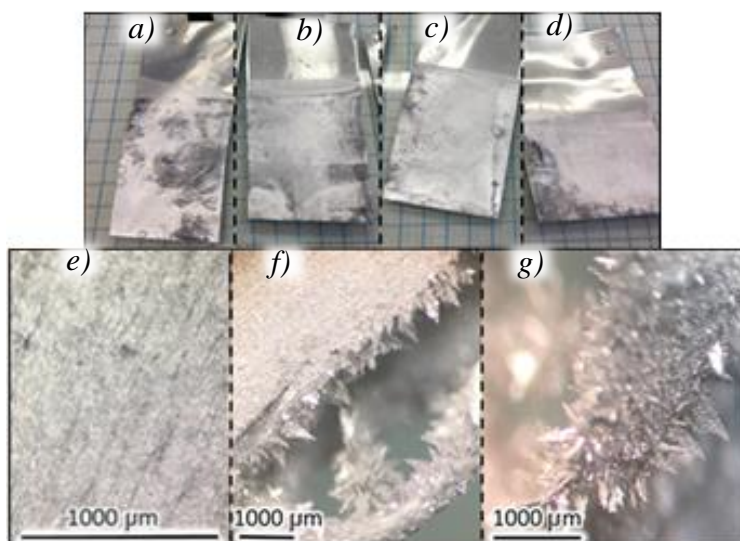


Figure 5. The macrophotographs (a, b, c, d) and microphotographs in the centre (e) and at the edges (f, g) of the cemented indium layer on Zn.

The In layer deposited on Zn completely covers the entire surface of the Zn, blocking the In^{3+} ions from the electron supply. At the central area (Fig. 5.e) the deposited In is quite smooth, while at the edges (Fig. 5.f,g) relatively large dendrites are formed. In contrast, when cementation is conducted on Al, the produced sponge is highly porous - due to a sufficient amount H_2 - and can be removed easily from the surface. The evolved hydrogen can rapture the produced sponge and ensure local stirring near the reaction front. This is shown in Fig. 6.

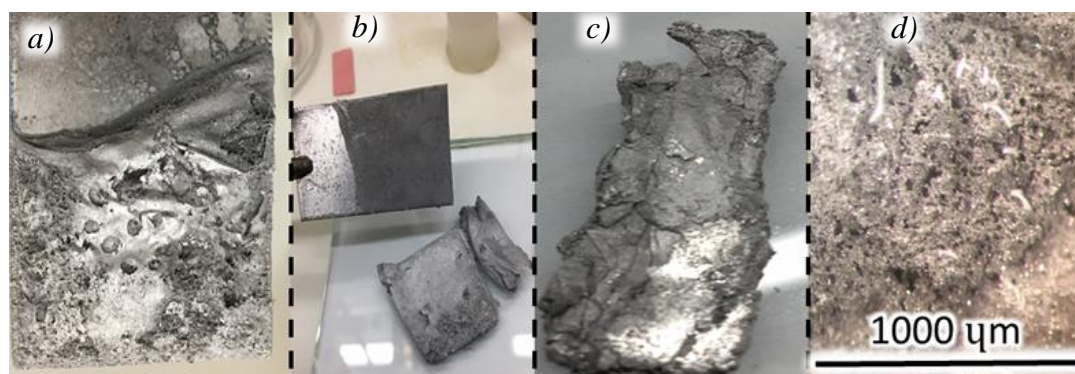


Figure 6. The photographs of indium cemented on Al: a)- the produced sponge, b)- removal of the sponge, c)- compacted sponge, d)- the microstructure of the sponge.

The freshly reduced sponge can appear quite metallic, when cemented at low temperatures and at high pH. However, even when the surface roughens and the products appear to be grey, compacting can reveal a metallic lustre.

A difference in morphology may also be explained by the differences in the equilibrium electrode potentials. While the difference in the standard electrode potentials of Zn and indium is -0.42 V, this is -1.33 V for Al. The cementation on Zn proceeds at much higher potentials and H_2 has a large overpotential on Zn, thus the produced layer is smooth and adheres to the surface. The cementation process was further examined by chronopotentiometry. It can be seen in Fig. 7 that at the first stage, the mixed potential expressed relative to the standard hydrogen electrode potential (vs. SHE) shifts toward the equilibrium electrode potential of the reducing agent in the given solutions. However, as the surface is increasingly covered with indium, its potential becomes dominant.

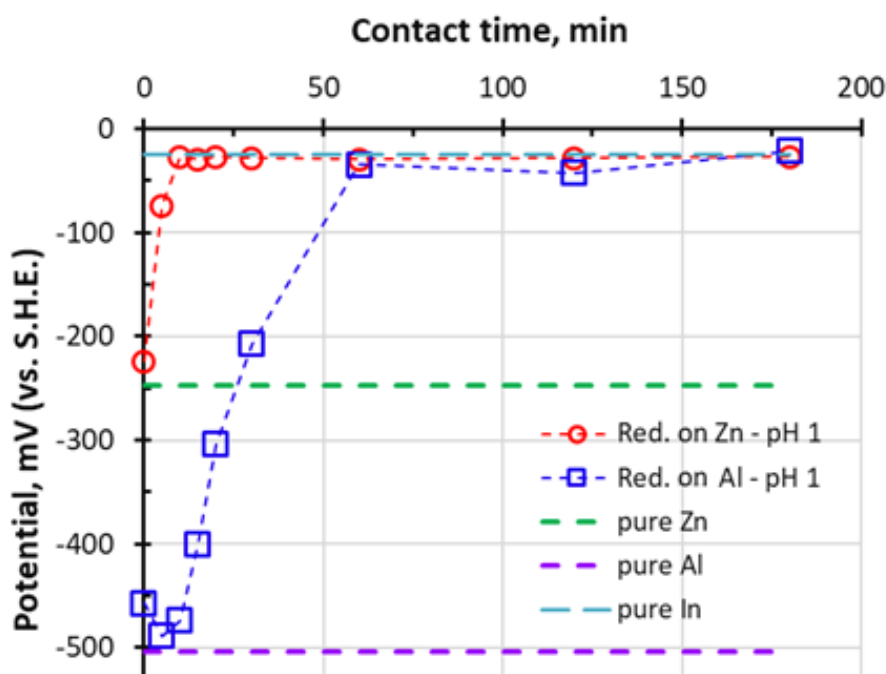


Figure 7. Chronopotentiograms of indium cementation with Al and Zn, respectively.

In the case of Al this process is seemingly slower as the In layer is porous and constantly raptured by the intense H_2 evolution. With Zn on the other hand, the electrode potential of the dense In surface immediately becomes dominant. These findings confirm the visual observations and justify the practical choice of aluminium as the more suitable reducing agent.

Regarding aluminium as the preferred reducing agent, the kinetics of the cementation and the reagent consumption at different temperatures and pH values can be seen at Fig. 8. The Al consumption at 55 °C and pH 0.5 - 1 roughly corresponds to the stoichiometric requirement. Evidently, at lower pH values the chemical dissolution of Al – as a side reaction – may become dominant, causing much higher Al consumption. Increasing the temperature, on the other hand, does not increase the Al consumption, however, it can speed up the process significantly.

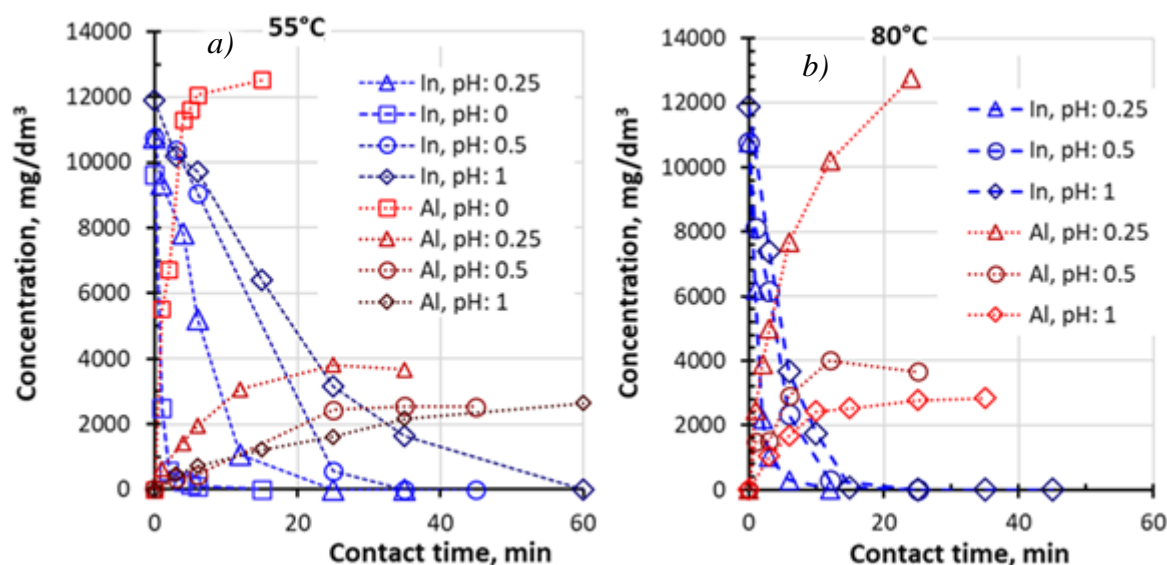


Figure 8. The kinetic characteristics of In cementation on Al at different pH settings and at 55°C (a) or 80°C (b) temperatures.

Another important characteristic is the purity of the reduced metal. In order to examine this aspect in practice, the produced indium sponges were removed from the surface and were pickled with 1M HCl for 1 hour to remove any residual reagent and impurity. The sponge was then compacted and induction-melted under vacuum, then fully dissolved in cc. HCl. This was followed by AAS analysis. Results are given in Table 1.

Table 1. The purity of the produced sponge (starting material 99.999% In)

Red. agent	Concentration, %						
	In	Al	Cu	Fe	Ni	Pb	Zn
Al	99.997	0.0014	0.000024	0.00174	0.000017	0.00001	0.000019
Zn	99.312	0.00002	0.000011	0.00021	0.00001	0.00011	0.687

It can be seen, that the purity of the metal that was reduced with Al is much higher, however iron is a serious contaminant, which largely comes from the smelter grade Al. On the other hand, the metal reduced with Zn contains high levels of the cementing metal, firstly because the In layer cannot be easily separated from the Zn, and secondly because the equilibrium Zn concentration in the In-Zn eutectic is rather high, while Fe is barely soluble at such low temperatures.

5. Conclusions

Cementing indium from a chloride solutions was examined thermodynamically and experimentally as well. Although theoretically the reaction can proceed with Fe, Zn, Mn, Al and Mg as well, the experiments revealed that Fe is unsuitable as a reducing agent. On the other hand, cementation proceeds quite quickly with the other examined metals as reducing agents. While Zn can only reduce a portion of the In before being covered with a dense layer of In, Al and Mg can remove In from the solution

completely. However, the reaction with Mg is too intensive for practical applications, excessively reaction heat and enormous amounts of H₂ evolved, causing also a significant explosion hazard. On the other hand, indium can be removed effectively from solution by cementation at the surface of an Al sheet. The produced metal sponge is quite porous thus it can be removed from the surface and can be subsequently melted. It was found that the impurities of the Al do not contaminate the produced sponge in a significant manner.

6. Acknowledgement

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