A FUNDAMENTAL STUDY OF COBALT CEMENTATION WITH ZINC DUST
IN THE PRESENCE OF COPPER AND ANTIMONY ADDITIVES

by

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M.Sc., Delft University of Technology, The Netherlands, 1992

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

Department of Metals and Materials Engineering

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

March 1995

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ABSTRACT

The mechanism of copper-antimony activated cementation of cobalt by zinc dust from a zinc electrolyte has been determined. The influence of process parameters on cobalt cementation was also studied. Both kinetic experiments and electrochemical investigations of the reduction of cobalt were used to investigate these aspects. The kinetic study was done using a batch cementation reactor and a non-steady state electrochemical cell. Electrochemical investigations were carried out in a steady-state electrochemical cell, focusing on current-plating potential relationship, deposit composition and morphology.

The difficulty in cementing cobalt by zinc dust from a zinc electrolyte, is attributed to the inhibition of cobalt reduction by zinc ions. In the presence of zinc ions, cobalt cannot be deposited in a pure form, but is deposited as a cobalt-zinc alloy which consists primarily of underpotentially deposited zinc. The addition of soluble copper and antimony to the electrolyte improves the rate and extent of cobalt cementation. Copper and antimony cement out of solution in the early stages of the cementation process, forming a preferential substrate for cobalt deposition. Copper increases the cathodic surface of the dust many times by depositing as a dendritic precipitate. Antimony as a cathodic substrate increases the cobalt content of the cobalt-zinc alloy. The antimony used in cementation forms numerous small cathodic sites on the dust surface, onto which a cobalt-zinc alloy with an increased cobalt content can nucleate. While these nuclei grow, their increased cobalt content is maintained. Copper-antimony activated cobalt deposition is under chemical or electrochemical control with an activation energy of 65 kJ/mole.

Higher temperatures increase the cobalt content of the cobalt-zinc alloy and consequently the kinetics of cobalt removal. However, the competing reaction of hydrogen evolution may also become severe, which leads to a high consumption of zinc dust. The solution pH does not affect the composition of the cobalt-zinc alloy, but a low concentration of free acid reduces the competition from the hydrogen evolution reaction, which takes place at the expense of cobalt reduction. Increasing the pH beyond the stage where basic zinc compounds form, does not inhibit the reduction of cobalt. The presence of organics in the electrolyte interferes strongly with cobalt deposition by adsorbing on cathodic sites. This lowers the cobalt content of the cobalt-zinc alloy and consequently the kinetics of cobalt removal from solution.

SAMENVATTING

In deze studie is het reactiemechanisme van koper-antimoon geactiveerde kobaltcementatie met zinkpoeder in zinkelektrolyet bepaald. Daarnaast is het effect van procesparameters op de cementatie van kobalt onderzocht. Hiervoor zijn kinetische en elektrochemische methoden naar de reductie van kobalt aangewend. De kinetische studie is uitgevoerd in een batch-cementatiereactor en een non-steady electrochemische cel. Elektrochemische onderzoeken aan de samenstelling en de kristalvorm van het precipitaat en de relatie tussen de kathodische stroomdichtheid en de reductiepotentiaal zijn uitgevoerd in een steady-state elektrochemische cel.

De problemen van het de cemenatie van kobalt met zinkpoeder uit een zinkelektrolyet zijn te wijden aan de verhindering van kobaltreductie door zinkionen. In de aanwezigheid van zinkionen wordt kobalt niet neergeslagen in de zuivere vorm maar vormt een kobalt-zinklegering die voornamelijk uit onderpotentiaal neergeslagen zink bestaat. De toevoeging van koper- en antimoonionen aan de oplossing verbetert de mate en de kinetiek van kobaltcementatie. Koper en antimoon slaan in de beginfase van het proces neer waardoor een voorkeurssubstraat voor de reductie van kobalt gevormd wordt. Koper slaat neer als fijne dendrieten en vergroot daardoor het kathodische oppervlak. Antimoon vormt kleine cathodesubstraten op het door koper vergrootte poederoppervlak, waarop nucleï van een cobalt-zinklegering met verhoogd kobaltgehalte kunnen nucleëren. Tijdens verdere groei behouden deze nucleï hun hoge kobaltgehalte. De koper-antimoon geactiveerde kobaltreductie is een chemisch of electrochemisch geactiveerd proces met een activatieenergie van 65 kJ/mole.

Een hoge temperatuur verhoogt het kobaltgehalte van de kobalt-zinklegering en daarmee de kinetiek van de kobaltreductie. Echter, het kan ook de parasitische reductie van waterstof verhogen wat leidt tot een hoger verbruik van zinkpoeder. De oplossings-pH heeft geen effect op de samenstelling van de kobalt-zinklegering, hoewel een lage concentratie van vrije waterstofionen de waterstofgasvorming, die ten koste gaat van kobaltreductie verlaagt. De vorming van alkalische zinkprodukten bij een verhoogde pH heeft geen effect op de kobaltreductie. Organische componenten die adsorberen aan de kathode verhinderen het neerslaan van kobalt door te adsorptie aan de kathode. Dit verlaagt het kobaltgehalte van de kobalt-zinklegering en daardoor de kinetiek van kobaltverwijdering.

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LIST OF SYMBOLS

a_i	activity of species i
A	active cathodic surface area; cm^2
C	concentration of reactant; mole/cm^3
C_o	concentration of reactant at time zero; mole/cm^3
C_t	concentration of reactant at time t; mole/cm^3
C_p	heat capacity; $\text{J}/\text{mole K}$ or $\text{cal}/\text{mole K}$
$ \overline{C_p} $	average heat capacity; $\text{J}/\text{mole K}$ or $\text{cal}/\text{mole K}$
E	potential versus a reference electrode; V
E°	standard potential versus a reference electrode; V
E_C	cathode potential versus a reference electrode; V
E_A	anode potential versus a reference electrode; V
E_{CELL}	cell potential; V
E_a	activation energy, J/mole or cal/mole
F	Faraday constant; $96500 \text{ C}/\text{mole}$
ΔG°	standard free energy change; J/mole or cal/mole
ΔG_{CELL}	free energy change of cell reaction; J/mole or cal/mole
k	reaction rate constant; $(\text{mol}/\text{cm}^3)^{1-n}/\text{sec}$
k_s	reaction rate constant; $(\text{mol}/\text{cm}^3)^{1-n} \text{ cm}/\text{sec}$
K	equilibrium constant
n	number of electrons involved in electrode reaction *)
n	order of reaction *)
R	ideal gas constant; $8.314 \text{ J}/\text{mol K}$
S°_{conv}	standard entropy; $\text{J}/\text{mole K}$ or $\text{cal}/\text{mole K}$
S°_{abs}	absolute standard entropy; $\text{J}/\text{mole K}$ or $\text{cal}/\text{mole K}$
t	time; sec
T	temperature; K

V solution volume; cm^3

z ionic charge

*) Correct use of symbol follows from the context.

ACKNOWLEDGMENTS

This research project would not have been possible without the help of a great number of people. First of all, I would like to thank Prof.Dr. D.B. Dreisinger for being my supervisor. The co-supervision of Prof.Dr. W.C. Cooper is also greatly appreciated. I am very grateful to Mr. P. McIver of the research department of Cominco Ltd., Trail, B.C. for the technical and financial support received from Cominco Ltd.. I would also like to acknowledge Ms. M. Mager for her assistance in the microscopic investigations. Thanks to my fellow graduate students and staff of the hydrometallurgy group for their assistance in various areas, and with whom I enjoyed working with.

Dedicated to my sister Diekske:

Kiezen is moeilijk Bollie

1 INTRODUCTION

Most of today's zinc is produced hydrometallurgically through the electrowinning of zinc sulphate electrolytes. This process generally consists of four major steps. First, zinc ores are roasted in order to convert the insoluble zinc sulphide to soluble zinc oxide. These oxides are then leached with sulphuric acid. Undesired impurities in the electrolyte which were leached from the roasted ore are removed in a subsequent purification stage. Finally, zinc metal can be electrowon from the purified electrolyte.

Purification is a most critical operation since the purity of the electrolyte directly affects the quality of zinc being produced. In this operation, soluble metallic impurities which are more electropositive than zinc are removed. Insufficient removal lowers the quality of the electrowon zinc in two ways. Firstly, impurity metals can be codeposited with zinc thereby reducing the purity of the cathode zinc. Secondly, impurity metals can lower the overpotential of hydrogen evolution on zinc, resulting in an increased rate of the parasitic hydrogen evolution reaction. Excessive hydrogen evolution gives spongy zinc which is of lower quality and lowers the current efficiency of electrowinning.

The impurities are removed from solution by either hydrolysis (Fe, Hg, Ga, In, Pb, Sb, Sn) or cementation with zinc dust (Cu, Cd, Ge, As, Ni, Co). However, in spite of a high thermodynamic driving force, cobalt removal is very poor in the cementation stage where the other impurities are easily precipitated. Cobalt is removed in a separate cementation stage which requires an increased temperature and small additions of soluble antimony and copper or arsenic and copper. The process using antimony is often preferred because the reduction of arsenic may evolve the highly toxic arsine gas. Even though the process has been applied industrially for many decades, little is understood about the mechanism of enhanced cobalt cementation in the presence of copper and antimony. A better understanding of the cementation mechanism and the effect of process parameters on cobalt cementation is needed in order to apply the process optimally.

The objectives of this investigation were therefore twofold: firstly, to determine the role of copper and antimony on promoting cobalt cementation and secondly, to investigate the effect of process parameters on the reduction of cobalt.

The results of this research are presented as follows. A literature survey reviews industrial practice, general aspects of cementation and previous work on cobalt cementation by other researchers. This is followed by the formulation of the experimental approach, which is based on information from the literature. The experimental part consists of three separate sections, each covering a different aspect of cobalt removal. The equipment used, experimental procedures and results are discussed individually per section. Finally, conclusions and recommendations based on the present research are made.

2 LITERATURE REVIEW

2.1 Hydrometallurgical extraction of zinc

Most of the world's zinc is produced hydrometallurgically through the electrowinning of zinc sulphate electrolytes. The primary hydrometallurgical process is the Roast-Leach-Electrowin process (RLE). The RLE process consists of four major steps: roasting, leaching, purification and electrowinning. Figure 2.1 shows one of the possible schematics of the process which is applied by Cominco Ltd., Trail, B.C.. However, the sequence of the cementation stages and type of additives may vary from plant to plant.

First, zinc sulphide concentrates are roasted in air at 800-975 °C to convert the insoluble sulphides to acid soluble zinc oxides. However, impurity metals in the concentrate may also convert to soluble forms. The final products are sulphur dioxide gas and calcine, the roasted concentrate.

In the second step, the calcine is leached with an acidic spent electrolyte from the tankhouse which contains 130-190 g/L sulphuric acid. At some zinc plants, the zinc sulphide concentrate is pressure leached to yield a zinc sulphate solution.

The third step comprises the purification of the zinc electrolyte. Impure solutions can seriously affect the quality of the zinc and the current efficiency. Purification generally consists of hydrolysis and at least two cementation stages.

In the first purification stage, iron is removed from solution by precipitating it as a goethite or jarosite by adjusting the pH. Under the addition of calcine and return acid, the pH is adjusted to between 4.5 and 5.1, resulting in the hydrolysis of iron. Several other solubilized impurities such as copper, arsenic, antimony, germanium, selenium, tellurium and silica are coprecipitated with the iron.

The remaining impurities are removed by electrochemical precipitation with zinc metal, also known as cementation. Finely dispersed zinc dust is added to solution which reduces the metal ions to metallic phases onto the zinc dust surface. In the first cementation stage, the metal impurities cadmium, nickel, thallium and copper are removed. The operating temperature is 40-50 °C and this step is referred to as the 'cold stage'.

Cobalt is removed in the second cementation stage. The temperature is in excess of 70 °C and this step is also referred to as the 'hot stage'. Small amounts of soluble copper and antimony or copper and arsenic are added to the electrolyte prior to the addition of zinc dust. Cobalt removal is very poor without the use of these additives.

In the final stage, zinc is recovered from the purified electrolyte by electrowinning in the tankhouse. The sulphuric acid which is generated during electrowinning is then recycled to the leach.

Figure 2.1: Schematic of hydrometallurgical zinc extraction

2.2 Harmful effects of cobalt on zinc electrowinning

Of all metallic impurities in the zinc electrolyte, cobalt is the most difficult impurity to remove and has the most detrimental effect in electrowinning. Although purity requirements differ, most plants tolerate less than 1 ppm cobalt in the tankhouse electrolyte. Depending on the composition of the electrolyte, the maximum allowed cobalt concentration can be as low as 0.3 ppm [1]. The negative effect of cobalt in the electrowinning of zinc is twofold [2-6]. Firstly, cobalt lowers the quality of the zinc deposit by causing round holes to form in the zinc deposit. These holes are formed by dissolution of the zinc deposit caused by increased hydrogen evolution on local zinc-cobalt galvanic cells. Secondly, the current efficiency is reduced because of increased hydrogen evolution. Zinc has a high overpotential for hydrogen evolution and can therefore be won at a high current efficiency. Because cobalt has a low hydrogen overpotential, it can act as catalyst for hydrogen evolution at the expense of zinc deposition.

The amount of cobalt which can be tolerated in the tankhouse is also dependent on the presence of other impurities because synergistic effects can occur [7-10]. Figure 2.2 shows the effect of the simultaneous presence of cobalt and antimony on the current efficiency of zinc electrowinning [10].

Figure 2.2: Synergistic effect of cobalt and antimony on the current efficiency of zinc electrowinning. Zinc electrowon from industrial acid sulphate electrolyte at 430 A/m² for 1 hour [10].

2.3 Theoretical aspects of cobalt cementation with zinc dust

Zinc metal can be used to remove more electropositive metal ions from the zinc electrolyte by cementation. The more noble ion is reduced onto the zinc particle under the uptake of electrons from the zinc dust which dissolves. The thermodynamic driving force of this reaction is the difference between the electrochemical potential of the zinc and of the precipitating metal impurity.

The general form of the reduction of a metal ion to its metallic form can be represented by:

Its reversible potential is given by the Nernst equation:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_M}{a_{M^{n+}}} \quad (2.6)$$

If the metal is reduced to its standard form, the activity of the metal can be taken as unity.

Then the reversible potential can be expressed as:

$$E = E^\circ - \frac{RT}{nF} \ln a_{M^{n+}} \quad (2.7)$$

The relation between the standard free energy change and the standard electrode potential is:

$$E^\circ = -\frac{\Delta G^\circ}{nF} \quad (2.8)$$

The following formula represents the general cementation reaction, with M as the precipitating impurity and N as the reductant:

The free energy change for the cell reaction equals the difference between the free energy of the reaction products and its reagents:

$$\Delta G_{\text{cell}} = n \Delta G_{\text{N}^{m+}} - m \Delta G_{\text{M}^{n+}} \quad (2.10)$$

The cell potential can be derived from the free energy change of the cell reaction or from the potential difference between the cathodic and the anodic reactions:

$$E_{\text{CELL}} = -\frac{\Delta G_{\text{CELL}}}{nF} \quad (2.11)$$

$$= E_{\text{C}} - E_{\text{A}} \quad (2.12)$$

The higher the change in free energy for the reaction, the higher the thermodynamic driving force for the reaction to take place.

Table 2.1 shows the electrochemical potentials of the individual reactants in the cementation of cobalt by zinc in a copper-antimony activated system. According to these results, the thermodynamic driving force for the species to be reduced onto zinc increases in the order of cobalt < hydrogen < antimony < copper.

Table 2.1: Electrochemical potentials of individual reactants in copper-antimony activated cobalt cementation. Conditions: 150 g/L Zn, 30 ppm Co, 30 ppm Cu, 1.5 ppm Sb, pH 4, 73 °C.

Electrochemical reaction	Concentration	Potential (mV _{SHE})	Potential difference with zinc (mV)
$\text{Cu} + 2\text{e} \rightarrow \text{Cu}$	30 ppm	210	971
$\text{SbO}^+ + 2\text{H}^+ + 3\text{e} \rightarrow \text{Sb} + \text{H}_2\text{O}$	1.5 ppm	-22	739
$2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2$	pH 4	-248	513
$\text{Co}^{2+} + 2\text{e} \rightarrow \text{Co}$	30 ppm	-411	350
$\text{Zn}^{2+} + 2\text{e} \rightarrow \text{Zn}$	150 g/L	-761	-

2.3.1 Rate processes in cementation

Many cementation reactions which are thermodynamically very favorable, rarely approach equilibrium condition in practice. When the reaction does not proceed in spite of a highly favorable negative free energy of the reaction, then the extent of reaction is determined by kinetics rather than by thermodynamics.

Cementation reactions are heterogeneous electrochemical reactions, the actual deposition occurring on a cathodic site, separated from the anodic zinc dissolution sites. Figure 2.3 depicts the stages of cementation of an impurity metal by zinc dust [11].

Figure 2.3: Stages in the cementation reaction of an impurity metal by zinc dust [11]

The cementation reaction can be thought of as taking place via a number of steps (Figure 2.3):

- 1 Transport of ions of the deposition metal M^{2+} from the bulk of the solution to the metal-solution interface through the liquid boundary layer
- 2 Conductance of electrons from the anodic dissolving zinc to the cathodic sites through the cemented deposit and electron transfer
- 3 Dehydration of the depositing metal M and incorporation of the atoms of deposited metal M into the crystal lattice
- 4 Release of Zn^{2+} ions from their anodic sites and hydration
- 5 transfer of Zn^{2+} ions into the solution through the deposit layer
- 6 Transfer of Zn^{2+} ions into the bulk of the solution through the liquid boundary layer.

Of the above steps, 1, 5, and 6 are under mass transfer control. Step 2, 3 and 4 are under chemical or electrochemical control. The actual rate at which the reaction proceeds depends on all of these steps although it is likely that one, or maybe two steps are rate controlling. Thus the reaction can be under chemical, electrochemical, mass transfer or mixed control. It is not possible that the overall rate can exceed the rate of the slowest step and a substantial increase in rate can only be achieved by increasing the rate of the slowest step(s) [12].

2.3.2 Cementation kinetics

The general expression for the rate of a monomolecular cementation reaction can be expressed by the following formula:

$$\frac{dC}{dt} = kC^n \quad (2.13)$$

The rate constant of the species which is reduced depends on the ratio of the active cathodic surface area to the solution volume.

$$k = k_* \left(\frac{A}{V} \right) \quad (2.14)$$

For first order reactions ($n=1$), the reaction rate of the species cementing from solution onto the zinc dust can be calculated as follows:

$$\frac{dC}{dt} = kC \quad (2.15)$$

$$\frac{dC}{C} = kdt \quad (2.16)$$

$$\ln \frac{C_t}{C_o} = -kt \quad (2.17)$$

$$k = -\frac{\ln \frac{C_t}{C_o}}{t} \quad (2.18)$$

For second order reactions ($n=2$), the reaction rate becomes:

$$\frac{dC}{dt} = kC^2 \quad (2.19)$$

$$\frac{dC}{C^2} = kdt \quad (2.20)$$

$$\left(\frac{1}{C_t} - \frac{1}{C_o} \right) = -kt \quad (2.21)$$

$$k = -\left(\frac{1}{C_o} - \frac{1}{C_t} \right) \frac{1}{t} \quad (2.22)$$

When a reaction takes place, its activation energy has to be overcome. The higher the activation energy, the more effect temperature has on the reaction rate. The dependency of the reaction rate on activation energy and temperature is given by the Arrhenius equation:

$$k \propto \exp\left(-\frac{E_a}{RT}\right) \quad (2.23)$$

An Arrhenius plot is obtained by plotting the natural logarithm of the experimentally derived reaction rates as a function of the reciprocal of the absolute temperature. The slope of the line which connects the datapoints multiplied by the gas constant gives the activation energy of the reaction.

E_a usually exceeds 40 kJ for a chemically or electrochemically controlled process and is less than 10 kJ for a diffusion controlled process [13]. The rate of a diffusion controlled cementation process increases with increased transport of the precipitation species. Increased agitation in the cementation reactor increases cementation rates under diffusion control but not of those under chemical control. An increase in temperature increases both the reaction rate of diffusion and chemically controlled processes, but has a more pronounced effect on chemically controlled processes.

Most cementation reactions follow first-order kinetics. The order of the reaction rate is independent of whether the reaction is under diffusion or chemical control. Cobalt and copper both follow first-order kinetic cementation rates when cemented on zinc dust. Copper cementation is under diffusion control [11] whereas cobalt is under chemical control [14]. The rate limiting step in the cementation of an impurity onto zinc can be either a slow step in the deposition of the impurity, the dissolution of zinc or the transfer of zinc ions through the deposit layer. Because cadmium and copper cementation proceeds at a faster rate and requires less zinc dust usage than cobalt [1,7], it is most likely that a slow step in the reduction of cobalt ions on the zinc dust determines the rate at which cobalt is deposited.

2.3.3 Hydrogen evolution

A competing reaction in the cementation of metal ions with zinc dust is the evolution of hydrogen gas by the reduction of hydrogen ions. In order to minimize hydrogen evolution, the concentration of hydrogen ions in solution should be minimized. However, too high a pH causes basic zinc compounds to form. These basic zinc compounds are thought to precipitate onto the zinc dust in the form of a basic zinc sulphates. The precipitates form an adherent insulating layer on the dust surface, inhibiting both zinc dissolution and metal reduction [1,14,15,16]. Other research contradicts the inhibiting precipitate phenomenon by showing cobalt cementation rates which increase with increasing pH, also at the stage at which basic zinc precipitates are formed [17]. A practical reason to prevent the formation of basic zinc sulphate precipitates is that they plug the filters which are used to separate the zinc dust from the purified electrolyte. The optimum acidity for cobalt cementation is a compromise between minimizing hydrogen evolution and the precipitation of basic zinc compounds. A typical solution acidity in cobalt cementation lies between pH 3.6 and 3.8. Because hydrogen evolution consumes hydrogen ions, the pH in the solution near the zinc dust surface is lower than that of the bulk solution.

Figure 2.4 shows the exchange current density of hydrogen discharge on various metals [18]. Typical metals with a low hydrogen overvoltage are nickel and cobalt, the latter is not shown in the graph but is in the vicinity of that of nickel. Metals with a high hydrogen overvoltage such as lead and zinc discharge hydrogen relatively easily at low polarisations. It has been suggested that antimony or antimony-copper precipitates on the zinc dust enhance cobalt reduction because it lowers the competing hydrogen evolution reaction, favoring cobalt reduction [14,15].

Figure 2.4: Exchange current density of hydrogen discharge on various metals [18]

2.4 Removal of cobalt by zinc dust cementation

Metallic impurities which are more noble than zinc can be removed from the zinc electrolyte by cementation with metallic zinc dust. Zinc in the form of dust with a typical particle diameter of 150 μm or less is added to the impure electrolyte. Fine dust is used in order to create a large surface area for reaction.

The reduction of cobalt with metallic zinc dust from a zinc electrolyte is very poor [12,19]. With equilibrium potentials of -0.28 V for cobalt and -0.76 V for zinc, it is expected that cobalt removal would be fast:

Despite the high theoretical thermodynamic driving force, cobalt does not cement onto zinc dust readily. A separate cementation stage at elevated temperatures is necessary to remove cobalt. However, even at these temperatures, cobalt removal from zinc electrolyte by zinc dust is very poor. It was found empirically that cementation could be improved considerably by using 'activators', additions to the electrolyte which improve cobalt cementation. These activators are usually a combination of either copper and antimony or copper and arsenic ions, which are added to the impure electrolyte before the zinc dust is added.

Currently, the copper-antimony and copper-arsenic processes are both applied industrially. The use of arsenic as an activator requires less zinc dust consumption than when antimony is used. However, the use of antimony may be preferred because it is potentially less toxic than arsenic [19]. The use of arsenic in the presence of metallic zinc can result in the formation of poisonous arsine gas.

2.4.1 Copper-arsenic process

In the copper-arsenic process, typical additions of copper and arsenic to the electrolyte are respectively 200 mg/L and 50-200 mg/L at a temperature in excess of 90 °C [1,12]. Figure 2.5 shows that arsenic and cobalt are cemented out of solution simultaneously. The cementation product has been defined as an alloy which codeposits under chemical control. Below 80 °C the alloy consists of CoAs [12,20], whereas at higher temperatures CoAs₂ is formed, independent of the initial Co/As ratio. Copper comes out before cobalt and deposits as pure copper and the alloy Cu₃As. Copper, cobalt and arsenic are deposited on the same sites on the zinc dust. Although copper does not alloy with cobalt, its addition improves the codeposition of arsenic and cobalt considerably [12,20,21]. It has been proposed that a galvanic cell is formed between zinc dust and copper particles. Cobalt is deposited on the copper by the galvanic current. Its deposition is improved considerably when it codeposits with arsenic [21].

2.4.2 Copper-antimony process

Cobalt cementation with copper-antimony activation requires more zinc dust than when copper-arsenic is used and proceeds at a slower rate [20]. Typical additions are 30 mg/l copper as copper sulphate and 1.5 mg/l antimony as antimony tartrate with 4 g/L zinc dust at a temperature of 72 °C [22]. It is the combination of the two metals which gives the best results. The addition of antimony only, improves the cementation of cobalt to a certain extent, whereas copper by itself has an almost negligible effect on the rate. Figure 2.6 shows the rates at which the individual species cement out in copper-antimony activated cobalt cementation. The important difference from the copper-arsenic process is that the activators cement out from solution at a faster rate than cobalt. Codeposition has been proposed due to the synergistic effect of copper and antimony on cobalt cementation; however, no alloys have been identified [15,16,20,23]. So far, the reaction mechanism remains unclear.

Figure 2.5: Removal rates in arsenic activated cementation [12]

Figure 2.6: Removal rates in antimony-copper activated cementation (copper and antimony depleted within 20 minutes) [14]

2.5 Inhibition of electrochemical cobalt removal

As has been mentioned before, the reduction of cobalt with metallic zinc dust from a zinc electrolyte in the absence of additives is very poor. Only when there is no zinc in solution, the removal of cobalt is significant. Figure 2.7 shows that the addition of only 1 g/L zinc ions to solution slows down the cobalt cementation kinetics considerably. In an industrial zinc electrolyte with a zinc content in the order of 150 g/L, this rate would become negligibly small.

Figure 2.7: Effect of the presence of zinc ions on the cementation of cobalt onto zinc [12]

The diagram is a phase diagram for the Koba-Zn system. The vertical axis is labeled 'Temperatur, °C' and ranges from 200 to 1000. The horizontal axis is labeled 'Kobalt, %' and ranges from 100 to 0 (Zn). The diagram shows several phase regions: $\alpha + \beta$, $\alpha + S$, β , $\beta + S$, $\beta_1 + S$, β_1 , $\beta_1 + \gamma$, γ , $\gamma + S$, $\gamma + \delta$, $\delta + S$, δ , $\delta + \epsilon$, $\epsilon + S$, ϵ , $\epsilon + \eta$, and $\zeta + \eta$. Key temperatures are marked at 925°, 966°, 924°, 895°, 746°, 675°, 566°, and 419.3°.

Graph showing the potential difference (V) versus composition (X) for the Fe-Fe₃C system. The y-axis ranges from 0.1 to 0.6 V. The x-axis ranges from 0 to 100% Fe₃C. The graph is divided into regions by vertical lines and shaded areas. Data points are plotted for three series: thermally treated alloys (circles), equilibrium alloys (squares), and electrolytic precipitates (dots). A curve connects the data points for the first two series, showing a decrease in potential difference as composition increases. The third series shows a sharp increase in potential difference at high compositions.

The Nernst equation for the alloy is similar to those for the pure metal phases. However, the difference is that the activity of the solid phase is not unity, but depends on the concentration of the metal in the alloy. Usually the activity of the metal in the alloy is taken as its mole fraction, providing it is not near an intermetallic phase boundary.

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2.5.1 Anomalous codeposition of cobalt and zinc

It has been well established that cobalt in the presence of zinc in solution, cannot be deposited as pure cobalt but is codeposited with zinc [24-29]. This is thought to be the most important cause for the inhibition of cobalt deposition by zinc ions. The formation of electrolytic alloys is usually limited to mixtures of metals whose potentials are not far apart. Therefore, the codeposition of cobalt with the much less noble zinc is not expected [30].

The deposition of cobalt-zinc alloys is called anomalous codeposition of zinc, since the less noble metal zinc is deposited preferentially over cobalt [31]. A second phenomenon that occurs during cobalt-zinc deposition is that zinc is deposited at a positive overpotential instead of a negative overpotential with respect to the reversible potential of zinc, also known as underpotential deposition of zinc. A recent publication by Gileadi [32] proposes that underpotential deposition is caused by the strength of the bond between the surface metal atoms and the depositing atoms. Underpotential deposition is usually observed when the less noble metal is deposited on a different substrate. The reversible potential of a metal refers to the free energy change in the discharge of metal ions which then become part of the crystal lattice.

Thus the free-energy change and the corresponding reversible potential refer to the formation of a bond between the depositing metal atom and an atom of the same metal on the surface.

Underpotential deposition can occur by the reduction of a metal on a surface of a different metal:

When the bonding between the foreign metal substrate and the depositing metal is more stable than the bonding between atoms of the same kind, metal deposition can take place at a potential more positive than expected. Although the above theory on underpotential deposition forms a plausible explanation, it has not been confirmed widely.

2.6 Mechanism of activated electrochemical cobalt removal

In spite of the potential difference between cobalt and zinc, cobalt removal from zinc electrolyte by zinc dust is very poor. In practice it was found empirically that the cementation could be improved considerably by using 'activators', additions to the electrolyte which improve cobalt cementation. The role of activators is to counteract the inhibiting effect of zinc and make cobalt cementation possible. The exact reaction role of the activators is not known. The following literature survey on copper-antimony and antimony activated cobalt cementation is divided into two sections. The first part deals with findings from cementation testwork and the second part discusses electrochemical and rotating disc experiments.

2.6.1 Cementation research

Blaser [33] performed a series of screening tests to determine the influence of temperature, amount of zinc dust, pH, Cu/Co ratio, Sb/Co ratio and cobalt concentration on the cobalt removal rate. Within the tested range, temperature had most influence on the rate, followed by Sb/Co ratio and amount of zinc dust. The Cu/Co ratio and pH were not of significant influence. Above a Cu/Co ratio of 1.0, the cementation was not improved further. It was suggested that copper does not codeposit with cobalt, but may function as a cathodic site for cobalt deposition.

Lew [14] tested the influence of various process parameters on the kinetics of cobalt cementation. Copper and antimony were removed during the early stages of cementation. There was an upper limit of copper and antimony additions above which cobalt cementation rates leveled off. With increasing temperature and increased zinc dust surface (higher loading or smaller dust), cobalt cementation was enhanced. Cobalt cementation was detrimentally effected by the presence of organics in solution. The cement layer on the zinc dust contained a mixture of cobalt, antimony and copper but consisted primarily of zinc (70-98 %). No alloys could be identified. The activation energy for cobalt deposition was 86.6 kJ/mole, which is typical for a chemically controlled process. It was suggested that copper and antimony form a substrate for cobalt reduction. The role of antimony was attributed to increasing the hydrogen overpotential on the surface, leading to a decrease in the competing hydrogen evolution and/or improving the stability

of the cobalt deposit towards dissolution. The cemented copper was thought to act as a cathodic site for cobalt deposition and increased hydrogen evolution due to its low hydrogen overpotential.

Kroleva [34] suggested that copper and antimony codeposit onto zinc dust as a Cu_2Sb alloy. Copper and antimony were cemented onto zinc dust from an aqueous solution containing copper sulphate and antimony tartrate in a ratio of 2:1. The copper-antimony coated zinc dust was separated from solution and used to cement cobalt from a zinc electrolyte. The Cu_2Sb alloy was claimed to form cathodic sites with a lowered overpotential for cobalt reduction and an increased overpotential for hydrogen generation. However, its formation was not verified by an analytical technique.

Fontana and Winand [23] studied the activation of cobalt with antimony and copper with the emphasis on the role of antimony. Without antimony, no cobalt was removed by zinc dust. Industrial cementation residues from solutions containing 250 mg/L copper, 10 mg/L antimony and 10 mg/L cobalt could not be identified in terms of the compounds formed. It was therefore decided to increase the concentrations of the impurities (e.g. 1 g/L cobalt) to have a better chance to detect compounds using X-ray fluorescence and diffraction. Characteristic lines of CoSb and CoSb_2 were found, although some of these lines were missing. Antimony lines were found as well, but no cobalt lines. In addition, there was a number of lines which could not be identified.

Fontana et al. [35] tested various alternatives for antimony. The criteria for the additives were: chemical properties similar to those of antimony, a sufficiently high reversible potential for deposition onto zinc and ability to form alloys with cobalt. The metals tested were tin, lead, arsenic and bismuth, which are known to form alloys with cobalt, save lead and bismuth. With the exception of bismuth, a certain degree of increase in cobalt removal was found for all metal additions. The cementation was further improved by addition of copper and/or cadmium. The presence of lead prevented the deposit from redissolution. The best kinetics were obtained for additive combinations containing arsenic or antimony. It was concluded that the promotional role of impurities on the cobalt cementation rate may not be attributed to alloy formation in all cases, since lead, which was one of the most beneficial species, does not alloy with cobalt. In addition, no alloys of any kind could be identified.

Adams and Chapman [1] used cadmium ions as an alternative for copper ions. The addition of 0.5-1 mg/L antimony remained indispensable for satisfactory cobalt removal. Higher antimony levels, as well as the presence of copper tended to redissolve cadmium. Cobalt cementation increased linearly with increasing cadmium addition. Similar to copper, cadmium had cemented out of solution onto the zinc dust in the early stages of cementation. The cementation rates of cobalt with cadmium-antimony activation compared favorably with the results from the copper-antimony process. In order to obtain similar performance with cadmium as a substitute for copper, higher additions are required with almost 400 mg/L cadmium versus 20 mg/L copper. An activation energy of 102.2 kJ/mole for cobalt removal was found, indicating that the process is under chemical control.

A 1972 Australian patent [36] claims that the addition of copper is not necessary for satisfactory cobalt removal. Very good results were obtained with the addition of 1.2 mg/L Sb_2O_3 at a temperature of 90 °C. It was found that the morphology of zinc dust followed by the addition of lead to the zinc has a large influence on the removal rate. Zinc dust which was produced by zinc vapor condensation removed cobalt faster than dust produced by dispersing a liquid jet of zinc. The presence of 1 % lead in the dust increased the cobalt and antimony removal further. The best cobalt removal was obtained by using zinc dust obtained from condensed zinc vapor which contained 1 % lead, followed by the same type of dust without lead. Cobalt removal was significantly less when the zinc dust was produced from a dispersed jet of zinc. This patent which was issued to Vieille Montagne (now: Union Miniere), provided an alternative to the conventional cementation process which requires both copper and antimony. However, presently copper is still used in their plant in Balen, Belgium.

The effect of the valence state of antimony ions on cobalt cementation has been studied by Cominco [37]. The antimony was added in three forms: Sb^{3+} as potassium antimony tartrate, Sb^{5+} as oxidized potassium tartrate and Sb^{5+} as the complex hexafluorantimonate. Cobalt removal was twice as fast with pentavalent antimony than with the trivalent form. It was suggested that the difference in performance is related to the relative rate of antimony reduction from the ionic to the metallic state. The faster the antimony ion is reduced to metal, the smaller the chance that it codeposits with the slower cementing cobalt ion. Whilst all trivalent antimony was cemented out of solution within an hour, there were still soluble antimony traces present when the pentavalent

forms were used. The cementate consisted of a spiked dendritic structure when trivalent antimony was used. With the addition of pentavalent antimony, the dust did not agglomerate as much and the deposit formed branched dendrites.

Aitkenhead [38] used finely powdered antimony metal as an alternative for soluble antimony. He found that all cobalt could be removed with as little as 0.002 mg/L antimony dust at 90 °C when no copper was present. Although copper is essential when soluble antimony is used, he found that only minute traces of copper were very detrimental where metallic antimony dust was used. He stated that the formation of a stoichiometric combination of a cobalt-antimony alloy was excluded, because this would involve compounds with at least six cobalt atoms to one antimony atom. It was suggested that antimony increases cobalt cementation by reducing the natural passivity of zinc caused by its hydrogen overvoltage.

An internal report by Cominco [39] comments on the possibility of using antimony metal without copper, based on results obtained by Aitkenhead [38]. The best results were obtained at the highest temperature; however, they were not as good as those based on the previous research. It was suggested that antimony reduces the hydrogen overpotential and/or formed cobalt antimonides. These antimonides cannot be stoichiometric compounds because of the high Co/Sb ratio. Instead, it was suggested that they may create active centers on the zinc dust surface. It was observed that with increasing antimony addition, the zinc did not agglomerate as much but remained better dispersed. With improved dispersion, the surface available for cobalt reduction is improved.

A 1972 US patent [40] claims the use of alloying additives to the zinc melt before it is dispersed into dust. This method provides an alternative for the conventional way of adding soluble antimony to the electrolyte. Zinc dust, alloyed with 0.002-5 % antimony and 0.05-10 % lead was produced by both distillation and atomization. The cobalt removal with the distilled type gave the best results, indicating that not only the composition of the dust but also particle morphology is of importance. It was proposed that antimony has a large affinity for cobalt, which results in improved cobalt removal. When antimony is present as an alloy component in the zinc dust, it forms a local galvanic cell with zinc wherein antimony acts as a cathode for cobalt reduction. The redissolution of deposited cobalt was thought to occur when all zinc had dissolved from the

particle, leaving cobalt and antimony as separate metallic phases. A local cell between cobalt and antimony is then formed, whereupon the precipitated cobalt dissolves. However, lead as an alloy component of the zinc dust saves zinc and antimony from contact with the electrolyte by enveloping them. Because lead is insoluble in zinc sulphate solution and electrochemically stable, the chance of formation of a local cell between cobalt and antimony is reduced.

A 1979 Russian patent [41] claims a further improvement of the above-mentioned US patent by the addition of graphite to the zinc dust. The zinc melt was alloyed with antimony and 0.1-5 % graphite before it was atomized into dust. It was claimed that without graphite in the dust, the electromotive force of the galvanic zinc-antimony pairs decreases due to the high polarization resistances and becomes insufficient for the reduction of cobalt. The addition of graphite to the zinc dust, increases the thermodynamic force between the cathode and anode reactions. Due to its porosity, it is likely that graphite increases the specific surface area of the zinc dust and thus the area available for cobalt deposition, but no comments were made on this aspect.

Internal reports by Cominco [42-43] comment on the use of manganese dust as an alternative for zinc dust. Because the reversible potential of manganese is 0.42 V more negative than that of zinc, it has a higher thermodynamic driving force for the reduction of cobalt. Copper and antimony were necessary additions, since virtually no cobalt was removed without them. The cobalt cementation rate was only three times faster when manganese dust was used instead of zinc. In addition, the required amount of dust was not reduced significantly.

Houlachi et al. [44] investigated the effect of common organics like flocculants, leveling agents and acid mist depressants on the cementation kinetics of cobalt. It was found that the various organics start slowing down the cobalt cementation rate at concentrations as low as 0.5 mg/L. In order to improve the performance of the cobalt kinetics in an organic-contaminated electrolyte, the antimony and copper concentrations and the zinc dust loading were adjusted. Increasing these parameters improves cobalt removal, but the interference by the organics could not be overcome completely in most cases.

2.6.2 Rotating disc and electrochemical research

Tozawa et al. [20] used a rotating zinc disc for the removal of cobalt. The ratios of Co:Sb:Cu in solution were 1:1:2. A potential-pH diagram of the Co-Sb-H₂O system was used to illustrate that formation of a stoichiometric CoSb alloy increases cobalt removal because it is more noble than cobalt. In the microscopic evaluation of the deposits, cobalt deposits were found around the copper-antimony precipitates but no CoSb alloy was observed.

Wang and O'Keefe [27] plated cobalt at high concentration from a zinc solution (80 g/L Zn, 5 g/L Co) at high current densities for galvanizing purposes. The addition of small amounts of antimony to the electrolyte increased the rate of cobalt deposition considerably. Concentrations as low as 5 mg/L raised the cobalt content of the deposit by a factor of 3 compared to the result when no antimony was added. The cobalt content of the cobalt-zinc deposit increased at higher agitation and lower current density. The promotional role of antimony on cobalt deposition was contributed to a catalytic effect. Antimony ions are known to catalyze cathodic reactions like hydrogen evolution in zinc electrowinning. It was suggested that antimony may modify the anomalous deposition of cobalt in a similar way.

Deblander et al. [16] electrodeposited combinations of copper, antimony and cobalt from zinc and aqueous solutions. They attributed the beneficial effect of copper and antimony to the codeposition with cobalt as alloys with reduced cobalt activity and increased nobility. It was stated that a ternary cobalt-antimony-copper alloy has an increased cementation rate. Its deposition would not be not inhibited by zinc ions and the alloy would exhibit a good resistance to corrosion by hydrogen evolution. A higher accelerating effect on cobalt removal was attributed to copper rather than to antimony because of its greater nobility. Antimony functions as a necessary addition because it stabilizes the alloy. Without zinc ions, the cobalt: antimony ratio in the deposit was almost 2:1. With zinc ions this was reduced to approximately 2:18 and zinc was the dominant species. They claimed that the metals deposit as Sb, Cu-Zn (brass), CoSb, CoSb₂ and a Cu-Co-Sb compound. However, in the presence of zinc ions, the only alloy which was identified was brass.

Fountoulakis [15] used a rotating disc to establish kinetic and electrochemical factors in cobalt deposition. The experiments were carried out without zinc ions in solution in order to simplify the mass balance. The overpotential of cobalt reduction was found to be independent of the substrate unlike that of hydrogen evolution which increased in the following order: cobalt, copper, antimony. Because of the high hydrogen evolution on pure cobalt, hydrogen evolution becomes the predominant cathode reaction at the expense of cobalt reduction. It was determined that copper and antimony ions enhance cobalt cementation by codepositing with cobalt as a ternary alloy with a higher hydrogen overvoltage and a higher nobility than pure cobalt. Antimony acts as a stabilizer by linking cobalt-antimony and copper-antimony alloys to one alloy and increases the hydrogen overpotential. Copper increases the nobility of the alloy, being the most noble constituent. At temperatures above 75 °C, cobalt deposition is under diffusion control with an activation energy of 13 kJ/mole. At lower temperatures, the activation energy increases to 27 kJ/mole bringing the reaction under mixed control. These values are remarkably lower than other reported activation energies [1,14] from experiments with zinc present in the solution. Because the effect of zinc ions in solution was neglected, the results of this research are questionable. Plenty of evidence has been brought forward to indicate that cobalt deposition is retarded due to the presence of zinc ions in solution [12,16,24,25,27,29].

Fontana and Winand [23] used an electrochemical cell with copper and antimony cathodes to remove cobalt from zinc electrolyte. The experiments were carried out potentiostatically, at potentials considerably more positive than the reversible potential of zinc. When no antimony was added to the solution, cobalt did not deposit. Increasing the cobalt concentration (1 g/L) did not show any cobalt deposition either. When antimony ions were added to the solution, cobalt did deposit from the solution with increased antimony concentration, but not from the solution with low cobalt. X-ray diffraction and fluorescence analysis identified the Sb and the alloys CoSb, CoSb₂, although some of the characteristic lines were absent. In addition, numerous unidentified lines were present as well. The authors proposed that antimony enhances cobalt deposition by reducing its overpotential. However, they also mentioned that it must be verified whether the reactions at increased cobalt concentrations are the same as at low cobalt levels.

2.7 Summary

In spite of the theoretical high thermodynamic driving force for cobalt removal by cementation with zinc dust, its removal is very poor. The addition of small amounts of copper and antimony to the electrolyte increases cobalt cementation significantly. There is an upper limit for the addition of copper and antimony, after which cobalt cementation does not improve further or levels off. Good results have also been obtained by the addition of antimony alone or by substituting copper by cadmium.

Beneficial effects on cobalt cementation include high temperatures because the process is under chemical control and is favored by a large zinc dust surface which is obtained by using a high zinc dust loading or fine dust. Adverse effects are caused by the presence of organics, which can slow down the kinetics considerably and too low a pH resulting in increased hydrogen evolution at the expense of cobalt deposition. The influence of a high pH has not been determined unequivocally, although it is claimed that zinc dust becomes passivated in an alkaline environment.

Several mechanisms have been proposed for this empirically found process of copper-antimony activation. Most of these mechanisms fall in the category of alloys and substrates. The activators would either form a preferential substrate for cobalt removal or codeposit with cobalt as a more noble alloy.

There are three reasons which may oppose the mechanism of ternary and binary alloy formation. Firstly, the cementation rate of cobalt is significantly lower than that of copper and antimony. Most of the cobalt cementation takes place when the activators have already cemented out. Secondly, no alloys of cobalt, antimony and copper have ever been found. In addition, the formation of stoichiometric cobalt-antimony and copper-antimony alloys is unlikely because antimony concentrations are comparatively too low. Finally, good cobalt removal has been achieved with antimony in the absence of copper.

Because copper and antimony deposit onto zinc dust well before most of the cobalt cementation takes place, it may be assumed that they form a preferential substrate for cobalt reduction. It is unlikely that the preferential copper-antimony substrate consists of a stoichiometric alloy, for

previously mentioned reasons. The substrate theory is strengthened by the fact that zinc dust alloyed with antimony has been shown to be a substitute for antimony additions to the electrolyte. However, an explanation has to be found to account for the fact that cobalt cementation continues after a first monolayer of cobalt has covered the preferential substrate.

The role of antimony ions as a catalyst should be questioned because antimony is reduced onto the zinc dust in the early stages of the cementation process.

2.8 Experimental approach

The objective of this research is to elucidate the mechanism of cobalt removal from zinc electrolyte by zinc dust cementation in the presence of antimony and copper. The experimental work consists of three sections. The following is a description of the approaches taken and a brief outline of how the results are presented.

In the first part, batch cementation tests were performed to determine the influence of copper and antimony on the kinetics of cobalt removal. The main objective was to determine whether cobalt is codeposited with copper and/or antimony as a more noble alloy or whether copper and antimony form a preferential substrate for cobalt deposition.

In the second part, the substrate effect was investigated further after it was established that copper-antimony activation is a substrate phenomenon. The influence of the cathode substrate on cobalt deposition was tested by using antimony and copper as cathode substrate materials. The morphology and the elemental composition cobalt-zinc deposits were studied as a function of common process parameters like temperature, antimony addition, and pH. Changes in electrolyte composition were negligible due to a low ratio of cathode surface area to electrolyte volume.

In the third part, a similar electrochemical cell but with larger cathodes was used. The experimental conditions followed the work with the smaller electrodes to supplement it with kinetic data and to verify the earlier proposed mechanism.

3 BATCH CEMENTATION OF COBALT

3.1 Introduction

This chapter deals with the cementation of cobalt from zinc electrolytes with zinc dust. The experiments were carried out in a batch reactor to simulate the industrial process on a small scale. In this kinetic study, the effect of copper and antimony on the cementation rates of cobalt were investigated. The objective was to study whether cobalt cementation is enhanced by the codeposition of cobalt alloys with increased nobility or whether antimony and copper form a preferential substrate onto which cobalt is deposited preferentially.

3.2 Experimental details

Batch cementation reactor

The experiments were conducted in a batch cementation reactor (Figure 3.1). The reactor consisted of a baffled 4-liter glass vessel, fitted with an acrylic lid with holes for sampling and instrumentation. The solution was stirred with an impeller at a rotation speed of 830 rpm. Continuous nitrogen sparging was employed to eliminate oxygen from the electrolyte, because oxidation of the precipitated cobalt by oxygen may result in cobalt redissolution [12]. The pH tended to rise during the course of the experiment. A pH controller was used for adjustment of the pH through the addition of sulphuric acid. A thermostatic temperature bath controlled the temperature of the solution at 73 ± 1 °C.

Solutions

The electrolyte used in these experiments was a purified zinc solution supplied by Cominco Ltd., Trail, B.C.. The zinc content was 155 g/L in the form of zinc sulphate and the pH was 3.6 (measured at 73 °C). For each experiment 3 liters of solution were used. Cobalt, copper and antimony were added to the electrolyte in the form of aqueous stock solutions. The additions of

these species to the electrolyte were respectively: 30 ppm cobalt (as $\text{CoSO}_4 \cdot 5\text{H}_2\text{O}$), 30 ppm copper (as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and 1.5 ppm antimony (as $\text{K}(\text{SbO})\text{C}_4\text{H}_6\text{O}_6 \cdot 1/2\text{H}_2\text{O}$).

Zinc dust

The zinc dust used was wet atomized dust with 1 % lead obtained from Cominco Ltd.. The dust was dry screened to the size range of -140+200 mesh. In each experiment, 4 g/L zinc dust was used.

Figure 3.1: Batch cementation reactor

3.2.1 Experiments

The zinc electrolyte was spiked with the additives cobalt, copper and/or antimony, prior to the cementation. The solution was heated to 73 °C, after which the pH was adjusted to pH 3.6 with sulphuric acid. The actual cementation experiment commenced at the time zinc dust was added to solution. The cementation was conducted for 120 minutes. In the course of the cementation time, the solution pH increased due to the evolution of hydrogen. A pH controller was used to prevent the pH from rising above pH 4.0 by the addition of sulphuric acid. Higher pH values are undesirable because they result in the precipitation of basic zinc compounds which cause difficulties in filtering the solution and may cause passivation of the dust [12]. The electrolyte was sampled for cobalt with a 25-mL pipet at time intervals of 15, 30, 45, 60 and 120 minutes after the initial zinc dust addition. Immediately after the samples were taken, they were air-pressure filtered. Copper and antimony samples were taken at shorter time intervals because their cementation rates were faster. The solution analyses were carried out by Cominco Analytical Services using atomic absorption spectrophotometry (AAS). At the end of the experiment, the cemented zinc dust was filtered and rinsed with distilled water for microscopic analysis.

The standard experiment in this chapter refers to cementation from an electrolyte which contains cobalt, copper and antimony before the zinc dust is added to the solution. This experiment is closest to industrial practice in which copper and antimony are added to the cobalt-containing electrolyte, to which zinc dust is then added.

3.3 Results and discussion

3.3.1 Activation with copper and antimony

The following four experiments show the effect of the addition of copper and antimony on the cementation of cobalt. The electrolyte contained cobalt and the additives copper and/or antimony before the zinc dust was added to the solution. Figure 3.2 shows the results, showing that cobalt removal follows first-order kinetics. Table 3.1 summarizes the effect of copper and antimony addition on cobalt cementation kinetics.

No activation

In this test, no copper or antimony was added to the solution. The cementation of cobalt was very poor, with less than 10 % of the cobalt being removed from solution.

Copper activation

The cobalt cementation rate was not improved by the addition of copper only. Although copper is desirable with the addition of antimony during the cementation of cobalt, it does not have a notable effect on its own. Within 30 minutes, all of the copper had cemented onto the zinc dust, leaving most of the cobalt in solution. This suggests that copper does not codeposit with cobalt.

Antimony activation

The addition of antimony only, had a notable effect on the cobalt cementation rate. The kinetics of the cobalt cementation rate increased by a factor of 3, compared to the two previous experiments in which no addition or only a copper addition was made. The antimony content in solution dropped quickly and most of the antimony was removed by the zinc dust within the first 30 minutes, maintaining a low level until the end of the experiment.

Copper-antimony activation

In this experiment, both copper and antimony were added to the electrolyte. This gave the best removal rate. Compared to experiments in which no addition was made, the cobalt removal rate increased by a factor of 18. The improved kinetics of the combined addition of copper and antimony are much better than the individual effect of these species. Figure 3.3 shows the fraction of copper, cobalt and antimony in the electrolyte as a function of cementation time. It can be seen that copper and antimony cement onto the zinc dust at a much faster rate than cobalt does. The results suggest that there is an interaction between copper and antimony in enhancing the removal of cobalt. Because copper and antimony precipitate onto the zinc dust in the early stages, they may form a preferential substrate on the zinc dust onto which cobalt is reduced.

Figure 3.2: Cobalt removal in the presence of copper and antimony additives.
Initial conditions: 30 ppm Co, 30 ppm Cu, 1.5 ppm Sb, pH 3.6, 73 °C, 4 g/L zinc dust.

Table 3.1: Rate of cobalt removal by cementation in the presence of copper and antimony additives. Initial conditions: 30 ppm Co, 30 ppm Cu, 1.5 ppm Sb, pH 3.6, 73 °C, 4 g/L zinc dust.

Additions	$k_{Co} \times 10^{-5}$ (s ⁻¹)	Normalized k_{Co}
none	1.8	1
copper	1.9	1.1
antimony	5.5	3
copper and antimony	32	18

Figure 3.3: Fractions of initial cobalt, copper and antimony concentrations in solution in standard test. Initial conditions: 30 ppm Co, 30 ppm Cu, 1.5 ppm Sb, pH 3.6, 73 °C, 4 g/L zinc dust.

3.3.2 Activation with sequential addition of copper and antimony

In the simultaneous addition of copper and antimony, it was found that copper and antimony were removed at a similar rate. It has been suggested that copper and antimony codeposit as an alloy [34] which acts as a preferential surface for cobalt reduction. In order to test whether the similar removal rate of the two species results in the codeposition of a copper-antimony alloy, copper and antimony were added sequentially in order to prevent possible codeposition in the following two experiments. In the first experiment, copper was the initial addition to the electrolyte, antimony and cobalt were added to solution after copper had cemented out of solution. In the second experiment, antimony was allowed to deplete first, after which copper and cobalt were added.

Figure 3.4 compares the cementation rate of copper in the pre-cementation stage with the standard experiment in which antimony and cobalt were added at the same time. The copper cementation rate follows first-order kinetics. The kinetic rate of copper is not affected by the presence of the other cementing species. Figure 3.5 shows that the antimony cementation rate follows second-order kinetics when it is the only addition to the electrolyte. In the presence of copper and cobalt, the kinetic rate is increased by a factor of 8 with a deviation in the first 20

minutes, in which the rate is initially lower and then gradually increases. This time interval corresponds to the time in which most copper cementation takes place. Initially, it may seem contradictory that the presence of copper increases antimony removal because it is an additional species which is reduced by zinc dust. However, copper is known to deposit as a highly dendritic precipitate when it is deposited at the limiting current density [11,45]. The dendritic structure increases the cathodic surface area of the zinc dust, resulting in a higher reaction area for antimony to deposit on. It is unlikely that the antimony removal rate is affected by cobalt cementation because cobalt is removed at a much slower rate and proceeds beyond the initial stage in which antimony is significantly affected by another depositing species.

For both experiments, the cobalt cementation rate was the same. This rate is identical to the standard experiment, in which cobalt, antimony and copper were present simultaneously in solution prior to zinc dust addition. The presence of either copper or antimony in solution does not affect the deposition of cobalt, which strongly suggests that copper-antimony activation is a substrate phenomenon.

Figure 3.4: Copper removal.

Initial conditions: 30 ppm Cu, pH 3.6, 73 °C, 4 g/L zinc dust.

Figure 3.5: Antimony removal.
Initial conditions: 1.5 ppm Sb, pH 3.6, 73 °C, 4 g/L zinc dust.

3.3.3 Activation with antimony metal

Aitkenhead suggested that antimony metal can enhance cobalt cementation [38]. He added minute fractions of finely ground antimony metal at a concentration of 0.002 g/L to the electrolyte. Copper was not added to the electrolyte because he found that it had a detrimental effect on the cobalt removal rate. In this experiment, finely ground antimony dust was added at concentrations of 0.010, 0.25 and 1.0 g/L without the addition of copper.

Figure 3.6 shows the cobalt removal kinetics. With the addition of 0.010 g/L antimony metal, the cobalt removal rate is similar to that for no activation. Only at higher antimony additions, do the cobalt kinetics start to improve. A solution analysis after 30 minutes showed an antimony content of 10 ppm for the experiment in which 1.0 g/L of antimony metal was used. A certain amount of antimony metal must dissolve, which can then be deposited onto the zinc. There is an induction time of approximately 15 minutes, before significant cobalt removal starts. It is likely that this time is related to the time it takes for antimony metal to dissolve. After this period, antimony acts similarly to when it is added directly in ionic form.

Figure 3.6: Cobalt removal with antimony dust additions.
Initial conditions: 30 ppm Co, pH 3.6, 73 °C, 4 g/L zinc dust.

3.3.4 Cementation with copper-antimony activated zinc dust

The previous experiments have shown that the kinetics of copper and antimony cementation are much faster than those for cobalt. It was also not necessary to have either copper or antimony in solution with cobalt as they cement out of solution quickly. This suggests that neither copper nor antimony codeposit with cobalt, but that they deposit onto the zinc dust surface, modifying the substrate for facilitating cobalt reduction. In the following experiment, copper and antimony were cemented onto zinc dust from a cobalt-free electrolyte. After all copper and antimony had been removed from solution, the zinc dust was removed from the electrolyte. It was thoroughly rinsed with distilled water and then air-dried. This dust was then used to remove cobalt from a copper-and-antimony-free electrolyte. Before the electrolyte was used, it was pre-cemented with zinc dust in order to remove any traces of copper and antimony.

Figure 3.7 shows that the cobalt removal rate is identical to that of the standard experiment in which cobalt, copper and antimony were present at the same time. Analysis of the solution showed that no redissolution of copper and antimony took place. From this result it can be

concluded that copper and antimony enhance cobalt cementation by depositing on the zinc dust surface, forming a preferential substrate for cobalt reduction.

Figure 3.7: Cobalt removal with copper and antimony added to the electrolyte and with copper and antimony activated zinc dust. Initial conditions: 30 ppm Co, pH 3.6, 73 °C, 30 ppm Cu, 1.5 ppm Sb, 4 g/L zinc dust.

3.3.5 Morphological analysis of cementation residues

From the cementation experiments, it was established that copper and antimony precipitate onto the dust prior to cobalt reduction to modify the zinc dust surface for cobalt deposition.

Subsequently, cobalt cementation can be divided into two phases. First, copper and antimony precipitate onto the zinc dust to form a new substrate. Then, cobalt is reduced onto this copper-antimony substrate. The following SEM pictures follow the transformation of the zinc dust surface during these stages. The elemental composition of the photographed zinc dust particles was analyzed with an X-ray energy dispersive spectrometer to verify that the morphology was characteristic for the species which were added to solution.

Figure p-3.1 shows the zinc dust used for all experiments before it was added to the electrolyte. The deviation of the zinc dust particle shape from sphericity and the shallow grooves on the dust surface cause a slight increase in the apparent surface area.

Figure p-3.2 shows the zinc dust after it has been cemented with copper and antimony. The activators have drastically changed the surface morphology. The cementate consists of numerous small nodules, the diameters of which are in the order of tenths of a micron. The finely grained deposit forms a new substrate on the zinc dust whose surface area is much higher than the initial zinc dust surface. This morphology is dominated by copper, which is the prime constituent of the deposit and which is known to form a highly dendritic precipitate when deposited at its limiting current density [12,45].

Figure p-3.3 shows the morphology of zinc dust which was pre-cemented with copper and antimony and then used to remove cobalt from a copper-and-antimony-free electrolyte. The cementate which was obtained from a solution in which cobalt, copper and antimony were present at the same time resulted in the same morphology (not shown). The morphology of the cementate looks very similar to that of the copper-antimony deposit. However, considering that the copper-antimony substrate is covered by an amount of cobalt approximately equal to that of copper, most of the visible nodules are cobalt deposits. The nodular form of the cobalt deposits is not a result of being deposited at its limiting current density as in the case of copper, because it is under chemical control. The change in dust shape and the corrosion holes are a result of excessive zinc dust consumption. Figure p-3.4 is a cross-section of the dust, which shows that the cementate is a very thin deposit with a thickness in the order of 1-2 μ . The corrosion of the zinc dust also appears in the form of dissolution gaps between the dust and the cementate. The corrosion can be partly attributed to the parasitic hydrogen evolution reaction which is catalyzed by the presence of cobalt.

3.4 Summary and conclusions

Batch cementation tests were used in a kinetic study of cobalt removal with zinc dust in the presence of copper and antimony to establish the mechanism of copper-antimony activated cobalt cementation. The objective was to study whether copper and antimony codeposit with cobalt as a more noble alloy or form a preferential surface for cobalt deposition. The following conclusions were reached:

The cementation of cobalt from zinc electrolyte by zinc dust is very poor. It can be improved by the addition of antimony and copper, species which activate cobalt cementation. Copper by itself does not have an effect on the rate, whereas antimony increases the cementation rate slightly. The addition of both copper and antimony gives the best result for increasing the rate of cobalt removal. The combined effect is larger than the sum of their individual effects.

The kinetic regime of cobalt and copper removal is first-order and antimony is second-order. Copper and antimony are depleted from solution at a faster rate than is cobalt. Within the early stages of cementation, copper and antimony are cemented out of solution onto the zinc dust, forming a precipitate onto which cobalt is deposited. Neither copper or antimony has to be in solution because they do not codeposit with cobalt as an alloy, instead they form a preferential substrate for cobalt reduction.

The copper-antimony deposit consists of a fine grained deposit, caused by deposition of copper at limiting current density. This deposit exhibits a larger surface area than that of the zinc dust. Cobalt deposits onto this substrate in the form of small nodules. The parasitic hydrogen evolution reaction results in additional zinc dust consumption.

4 ELECTROCHEMICAL COBALT REMOVAL: MECHANISTIC ASPECTS

4.1 Introduction

The results from the batch cementation experiments in the previous chapter led to the conclusion that copper and antimony form a preferential substrate on zinc dust, which enhances cobalt deposition. The main objective of this research was to understand the behavior of copper and antimony as preferential substrates for cobalt deposition from zinc electrolytes. Their effect on the composition and morphology of the deposit, the growth mechanism and the relation between current density and potential was studied. Secondly, the manner in which common process parameters like pH, temperature, organics etc. influenced morphology and deposit composition was examined. The results were compared with those from cementation experiments. The experimental apparatus was in the form of an electrochemical cell, which allowed for better defined parameters and control than in the batch cementation experiments. The solution composition was kept constant in order to eliminate the effect of changes in electrolyte composition on cobalt deposition.

4.2 Experimental details

Electrolytic cell

The electrolytic cell consisted of a 300-mL glass beaker fitted with a slotted Plexiglas lid (Figure 4.1). The distance between the anode and the cathode was 2 ± 0.5 cm. A platinum wire anode was placed in a glass fritted disc to prevent the evolving oxygen from diffusing into the electrolyte, because this is known to redissolve the deposited cobalt [12]. Nitrogen sparging was provided through a gas dispersion tube with a horizontally placed 20-mm coarse glass fritted disc on the bottom of the cell below the cathode. Its function was to provide mechanical stirring of the electrolyte and to eliminate dissolved oxygen from the solution. Sparging was commenced 15 minutes before the start of the experiment. 250 mL of solution was used for each experiment. Because the cathode surface area to solution volume was very small, the changes in the electrolyte

composition were negligible. The temperature was controlled by a constant temperature water bath at 73 ± 1 °C, unless otherwise stated. A Luggin capillary was placed 2 mm from the cathode surface. Potential differences between the cathode and a calomel electrode placed in the Luggin capillary were measured at room temperature. A Hokuto Denko galvanostat/potentiostat model HA-211 A supplied the power for the cell. The potential was recorded by a Keithley 171 digital multimeter which was connected to a chart recorder. The current was measured with a Circuit-Test DMR-2800 multimeter. Figure 4.2 shows a schematic of the experimental set-up.

Cathodes

Copper and antimony were used as cathode substrates. The cathodes were cut from commercial grade copper rod and machined to a diameter of 0.5 inch (1.27 cm). An insulated electrical wire was soldered at the back of each disc to provide electrical contact. The disc was mounted in resin, in such a way that only one side of the disc was exposed. The cathodes were polished to a smooth surface with 5 micron alumina grit. A small hole was drilled in the back of the mount to hold the Luggin capillary so that its tip was at a distance of 2-3 mm from the cathode surface. The antimony substrate was prepared by plating from a 0.2 M antimony tartrate solution onto a copper cathode at 75-100 A/m² for at minimum of 45 minutes. This generated an antimony layer with a thickness of several microns. Because the copper cathodes were subject to oxidation in the air, they were lightly polished immediately before the experiment to remove the thin oxide layer. Prior to the experiment, both copper and antimony cathodes were cleaned with 10 % HCl solution and rinsed with distilled water.

An attempt was made to plate the copper-antimony alloy Cu₂Sb, of which it has been said that this alloy forms the preferential substrate for cobalt reduction [34]. However, it was not possible to electrowin this alloy, neither at various molar ratios or different current densities. In addition to the results from the batch cementation experiments in the previous chapter, this strongly suggests that the proposed Cu₂Sb alloy does not form electrochemically.

Electrolyte

The electrolyte was a purified zinc electrolyte from Cominco Ltd. It was treated with activated carbon to remove any organics and contacted with zinc dust to remove traces of copper and antimony. The zinc content was 155 g/L and the pH was set to 3.0 (measured at 73 °C). For the cobalt removal experiments, the electrolyte was spiked with 30 ppm cobalt from an aqueous stock solution of cobalt sulphate ($\text{CoSO}_4 \cdot 5\text{H}_2\text{O}$). For experiments where antimony was required in the electrolyte, it was added from an aqueous solution of antimony tartrate ($\text{K}(\text{SbO})\text{C}_4\text{H}_6\text{O}_6 \cdot 0.5\text{H}_2\text{O}$).

Figure 4.1: Electrolytic cell.

Figure 4.2: Schematic of the set-up of the electrolytic cell.

4.2.1 Experiments

Determination of reversible potential of zinc

A copper electrode was plated with zinc for 5 minutes at 1000 A/m^2 . Thus the cathode became completely covered with a layer of zinc, so that it would behave as zinc cathode. Subsequently, the potential of the electrode was measured over a range of constant current densities. First, the current density was decreased stepwise to give potential readings for the deposition of zinc. Then, it was increased to positive values which gave dissolution potential data. By plotting the potential readings versus the current density, the polarization behavior of zinc can be presented. The reversible potential of zinc is obtained by extrapolating the current density to zero.

Galvanostatic cobalt deposition

The zinc electrolyte, spiked with 30 ppm cobalt was used for the deposition of cobalt. The cathode was plated at a constant current density between 10 and 50 A/m^2 . After a deposition time of 90 minutes, the cathode was removed from solution immediately and thoroughly rinsed with distilled water. The base line conditions for the experiments were: copper or antimony substrate, 30 A/m^2 , 73°C and pH 3.0.

The reason for carrying out the experiments galvanostatically instead of potentiostatically is that the potentials of the reactions occurring during cementation have a mixed potential depending on the initial substrate, the deposit forming over time with hydrogen evolution taking place on the substrates. Since these values were not known, it was decided to perform the experiments galvanostatically in a low current density range.

The morphology and composition of the cobalt deposits were analyzed by scanning electron microscopy (SEM) and X-ray energy dispersive spectrometry. The SEM uses a narrow beam to scan the sample surface. However, the penetration of the electron beam into the sample is much higher, which results in the generation of X-rays from an interaction volume of a typical bulbous shape with a diameter of the order of $1\text{-}2 \mu$. Because of the interaction volume, part of the

generated X-rays come from the underlying cathode substrate. For the quantitative analysis of the deposit, the X-ray intensity of the substrate was subtracted. In order to get a representative compositional analysis of the deposit, 7-10 different electrodeposits on the cathode were analyzed. The area around the edges of the cathode was not taken into account for analysis because the increased current density at the edges is not representative of the applied current density.

4.3 Results and discussion

4.3.1 Reversible potential of zinc

The polarization behavior of zinc is depicted in Figure 4.3, in which the potentials are plotted against the current density. Extrapolation of the curve to zero current density yields a potential of -0.955 V (vs. SCE). This value is the mixed value of the reversible potential of zinc and hydrogen reduction on zinc. However, because the hydrogen overpotential on zinc is very high and the acidity is moderate, the hydrogen evolution is low. The potential of -0.955 V at 155 g/L zinc and 73 °C was therefore taken as the reversible potential of zinc. The theoretical calculated potential (see Appendix C) gave a very close value for the reversible potential of zinc.

Figure 4.3: Polarization behavior of zinc. 155 g/L zinc, pH 3.0, 73 °C.

4.3.2 Cobalt deposition on copper substrate

Composition

In these experiments, a copper substrate was plated at current densities between 10 and 50 A/m². The objective was to study the role of copper as a substrate for cobalt deposition. Table 4.1 depicts the compositional analysis of the cathode deposit. The deposit on the copper substrate consisted of a cobalt-zinc alloy, containing mainly zinc with a small amount of cobalt. The cobalt content of the cobalt-zinc alloy decreased further with increasing current density. The plating potential was 20 to 40 mV more positive than the reversible potential of zinc. Because zinc deposition was the main reaction, followed by hydrogen, it was not possible to distinguish a trend between current density and plating potential.

Table 4.1: Cobalt content of cobalt-zinc deposits on copper substrate as a function of current density. 30 ppm Co, 73 °C, pH 3.0.

C.D. (A/m ²)	Co (wt. %)
10	1.1
20	0.5
30	0.4
40	0.3
50	0.2

Morphology

The deposit looked similar for the current densities applied. Figure p-4.1 shows the morphology of the deposit on a copper cathode obtained at 30 A/m². The crystals on the cathode are small and cover most the cathode surface.

4.3.3 Cobalt deposition on antimony substrate

Composition

Antimony was tested for its substrate characteristics in the deposition of cobalt in the same way as copper. The antimony cathodes were plated at current densities in the range of 10 to 50 A/m² for 90 minutes. The crystal growth of the deposit on antimony was followed over time in order to determine how the deposit is developed and whether time has an influence on the composition of the cobalt-zinc alloy. The experiments were performed by plating cathodes for 15, 30, 90 and 180 minutes at 30 A/m².

No deposit could be obtained at a current density of 15 A/m² and lower, only hydrogen was evolved. The lowest current density at which a deposit was formed was 20 A/m². The deposit consisted of a cobalt-zinc alloy with zinc as the prime constituent. However, the cobalt content of the deposit on an antimony cathode is approximately 10 times higher than that on a copper substrate. The cobalt content of the deposit on antimony showed a linear dependence on the current density, as depicted in Figure 4.4, with a lower cobalt content at higher current densities. Apparently, antimony increases the cobalt content of cobalt-zinc alloys in the anomalous codeposition behavior.

The difference between the plating potentials of the cobalt-zinc alloys on antimony and the reversible potential of zinc was 20-40 mV. These values are similar to those on the copper substrate, probably because the deposit contains mainly zinc and relatively little cobalt. At the lowest current densities, where no deposit was formed, the difference between the plating potentials and the reversible potential of zinc was more than 100 mV, even though the plating potential was more negative than the reversible potential of cobalt.

Figure 4.4: Cobalt content of cobalt-zinc deposits on copper and antimony substrates as a function of current density. 30 ppm Co, 73 °C, pH 3.0.

Morphology

The deposit morphology on the antimony cathode was remarkably different from the one on the copper substrate. The average size of the crystals was much larger and the spacing between the individual crystals was also larger. The surface coverage was very low compared to that on the copper substrate. The direction of growth was more perpendicular than parallel to the cathode substrate. The crystals could be distinguished with the naked eye as greyish spots on a predominantly bare antimony cathode. The growth tended to be concentrated on the development of existing nuclei instead of on the formation of nuclei. This may indicate that there is a high nucleation overpotential for the alloy on antimony. Below a certain current density, no deposit was formed on antimony unlike on copper, indicating a high overpotential.

After 15 minutes of plating, the first crystals had formed on the cathode. The deposits varied in size with a maximum diameter of 12 μm . At 30 minutes, the number of crystals had increased slightly. The existing deposits continued developing up to 50 μm . After 90 minutes of deposition, the largest crystals had diameters exceeding 80 μm . After 180 minutes, the crystals had expanded such that they started overlapping. Even at this stage, less than 20 % of the

antimony substrate was covered by the deposit. During the course of the plating experiments, more nuclei formed but most of the deposition was attributed to the development of the crystals which had formed in the early stages. The zinc:cobalt ratio of the cobalt-zinc alloy did not change during deposition.

The growth process indicates that antimony functions as a substrate onto which cobalt-zinc alloys with an increased cobalt content nucleate. Once a cobalt-rich nucleus is formed, it develops further to a crystal while maintaining its high cobalt content. The preference of cobalt to deposit on antimony may be due to the change in free energy when the initial nucleus is formed. The surface energy is an energy barrier which has to be overcome when a nucleus is created on a cathode. If the change in free energy for the nucleation of cobalt on antimony is much lower compared to zinc, copper and other substrates, a cobalt enrichment of the nucleus may be the result. These nuclei are the base for the crystals, which maintain the compositional characteristics of the initial nuclei as they grow.

Three different types of morphology could be distinguished: randomly oriented nodular deposits (Figure p-4.2) and six-sided polygons (Figure p-4.3). In addition, a combination of the two types occurred as well (Figure p-4.4). This consisted of an initially polygonal deposit which was deposited with a rough deposit in a later stage of deposition. Occasionally, all three types were found on the same cathode. There was no significant difference in alloy composition between the different crystal types occurring on a same cathode. Figure p-4.5 shows the formation of the three morphologies on the same cathode. The six-sided polygons are well-developed crystals. Other types of polygons were also observed. The growth was faceted with the slowest direction of growth parallel to the surface. The rough deposits had a random growth pattern from different growth sites and developed as randomly oriented nodules. The combination type consisted of well-developed crystals with rough deposits developing on top. The polygons grow layer-wise by the successive formation of steps on the facets. Steps and other imperfections, maybe in the form of adsorbed species or oxides, can facilitate the formation of rough crystals [46].

The morphology type was dependent on the current density at which the alloy was deposited. At increasing current density, the cobalt content of the deposit decreased which effected the morphology, as shown in Table 4.2. At the highest current density, both the polygonal shape and the nodular form occurred at the same frequency. At the lowest current density, the only morphology type occurring was the rough deposit. According to Yan [47], the morphology of electrodeposited cobalt-zinc alloys is dependent on the cobalt content. He stated that cobalt and zinc deposit as successive layers of cobalt and zinc which are of nanometer thickness. At a low cobalt content, the deposit appears in the form of a hexagonal deposit. As the cobalt content increases, the coherence between the layers is reduced due to lattice mismatch and the morphology becomes nodular.

Table 4.2: Cobalt content and morphology of cobalt-zinc deposits on antimony substrate as a function of current density. 30 ppm Co, 73 °C, pH 3.0.

C.D. (A/m ²)	Co (wt. %)	Deposit morphology
20	5.7	nodular
30	4.2	nodular/(hexagonal)
40	3.9	nodular/hexagonal
50	3.0	nodular/hexagonal

The nodular cobalt deposits on the antimony substrate have the same morphology as those on the copper-activated zinc dust. The size of the nodules is smaller on the dust than on the antimony substrate, which is most likely caused by the smoothness of the polished cathode surface, onto which nucleation is more difficult than on a surface with imperfections, like zinc dust. Therefore, the growth on the antimony substrate favors the development of the existing deposits over the formation of new nuclei. The polygonal deposits which were plated on the antimony substrate at current densities of 30 A/m² and higher, were not formed during cementation with zinc dust. Because this morphology is related to the deposit composition and therefore the plating current density, it may be that the cathodic current density on zinc dust is less than 30 A/m² at a temperature of 73 °C.

4.3.4 Effect of antimony addition

At this stage, it has been shown that cobalt is deposited preferentially on antimony, but not on copper. However, the presence of both copper and antimony enhances cobalt cementation by zinc dust to a larger extent than when only antimony is used. The objective of this experiment was to study whether antimony functions as a preferential cathodic site for the formation of the initial cobalt-rich cobalt-zinc nuclei and what is the function of copper. Instead of an antimony substrate, a copper electrode was used and 1.5 ppm antimony was added to the cobalt spiked electrolyte.

The cobalt-zinc alloy which had formed had the same increased cobalt content as that on a pure antimony substrate. The amount of deposited antimony on the electrode was very small with concentrations less than 0.5 wt. % and was at the background level on most parts of the cathode. This can be explained by the deposition of minute antimony spots on the copper substrate, which then act as preferential cathodic sites for the cobalt-rich nuclei. These nuclei develop to crystals, growing further on the copper substrate. This proves that the initial nucleus forms the base for the characteristics of the crystal.

4.3.5 Effect of temperature

Temperature is known to be one of the most critical parameters in cobalt cementation [33]. In practice, elevated temperatures are always used for cobalt cementation. Commonly, the process is operated above 70 °C because lower temperatures give poor cobalt removal. In this experiment, the effect of temperature at 50, 60, 73, 80, 85 and 90 °C was studied on an antimony substrate. The plating time was doubled for the experiment at 90 °C because the deposit was too thin for accurate compositional analysis by the SEM.

Table 4.3 lists the cobalt content of the deposit, the deposit morphology, and the plating potential as a function of temperature. In the 50 to 85 °C range, the cobalt content increases exponentially with temperature as shown in Figure 4.5. The increase in cobalt content and shift to more

positive potentials at 90 °C are substantially higher than expected from the results at lower temperatures.

Table 4.3: Cobalt content, morphology and plating potentials of cobalt-zinc deposits on antimony substrate as a function of temperature. 30 ppm Co, 30 A/m², pH 3.0.

Temperature (°C)	Co (wt. %)	Plating potential (Vsce)	Deposit morphology
50	1.0	-0.93	hexagonal
60	1.8	-0.93	hexagonal
73	4.2	-0.92	nodular(/hexagonal)
80	5.1	-0.91	nodular
85	8.8	-0.91	nodular
90	74	-0.80	smooth film

Figure 4.5: Cobalt content of cobalt-zinc deposits on antimony substrate as a function of temperature up to 85 °C. 30 ppm Co, 30 A/m², pH 3.0.

The morphology changed markedly with temperature, this change resulting from the cobalt content of the alloy [47]. At the lowest temperatures the deposit appears as a hexagonal deposit. The morphology is little influenced by cobalt because of its low content. Upon increasing the temperature, the deposits became nodular. The lattice mismatch between cobalt and zinc is more pronounced at the higher cobalt content, which makes the growth of well-developed crystals impossible. At the highest temperature, the electrodeposit consists of a smooth black deposit. At

this temperature, cobalt is the major constituent of the alloy and subsequently governs its morphology.

Figure p-4.6 and p-4.7 show cross-sections of two deposits, plated at 50 °C and 85 °C respectively. At the lower temperature, the cobalt content is only 1.0 wt. % and the morphology is polygonal, whereas at the higher temperature the cobalt content is 8.8 wt. % and the morphology is nodular. There is no visible layering or cluster formation within the deposits. An X-ray distribution dot map of cobalt and zinc of the cross-sections was taken to determine whether the cobalt-zinc ratio varied throughout the crystal. The low cobalt content of the low temperature polygonal deposit made it difficult to distinguish cobalt from the background response. The cobalt and zinc dot maps of the nodular deposit of Figure p-4.7 do not show areas which have a enrichment in either cobalt or zinc. Lower X-ray responses for both zinc and cobalt are related to the presence of pores in the deposit. There seems to be a slight decrease in cobalt concentration towards the top of the crystal. However, the difference between the specific density of the antimony substrate at the bottom and the epoxy resin also influences the intensity of the X-ray response. The dense antimony substrate increases the response around the interface between the deposit and the substrate, whereas the light epoxy surrounding the crystal reflects less electrons at the top compared to less than the average towards the middle of the deposit.

4.3.6 Effect of pH

Hydrogen ions compete with cobalt for the reduction by zinc dust. In order to minimize the parasitic hydrogen evolution reaction, the pH should be high. However, it is also claimed that the precipitation of basic zinc sulphates on the surface at too high a pH inhibits cobalt reduction [12,15,16]. In this experiment, the effect of electrolyte pH was studied at 1.5, 3.0 and 4.4. At the highest pH, the solution had a milky color, indicating the formation of basic zinc sulphate in solution.

For all pH values, the cobalt content of the deposits was the same. The deposit at pH 4.4 had a more dull appearance and also contained some sulphur, probably indicating the incorporation of a basic zinc sulphate in the cementate. At the lower pH values, the plating potentials were more

positive because of increased hydrogen evolution. Thus hydrogen ions in the electrolyte consume cathodic current at the expense of cobalt and zinc deposition, but do not affect the composition of the alloy.

4.3.7 Effect of organics

The presence of organics in the electrolyte slows down the kinetics of cobalt cementation [44]. Organic additives can adsorb on the cathode changing the electrode reactions. In this experiment, 3 ppm of the organic Percol 338 was added to the electrolyte to examine how cobalt deposition is inhibited. Percol 338 is a flocculant which is used in earlier stages of purification to flocculate the hydrolyzed iron compounds which facilitates their removal.

Table 4.4 compares the cobalt contents of the deposits on the antimony substrate with organic addition, with the antimony and copper substrates without organic addition. It can be seen that the organic has a strong inhibiting effect on the deposition of cobalt. While antimony increases the cobalt content in the anomalous codeposition as shown in the previous experiments, this effect is eliminated upon the addition of organic. In the presence of organic, the deposit on antimony has the same cobalt content as on copper. The theory, which has been developed during this research, proposes that a low surface energy barrier between cobalt and antimony promotes the deposition of cobalt. When organics adsorb on the antimony surface, this barrier is increased due to the need of electron transfer through the adsorbed organic layer.

Table 4.4: Cobalt content of cobalt-zinc deposits with and without the presence of organics. Organic: 3 ppm organic Percol 338. 30 ppm Co, 30 A/m², 73 °C, pH 3.0.

Substrate	Organic addition	Co (wt.%)
antimony	none	4.2
antimony	yes	0.4
copper	none	0.4

The electrode coverage with the organic was similar to that without the organic, indicating that only the deposition of cobalt and not that of zinc was inhibited by the organic. The adsorption of organics on active growth sites disturbed the growth of the polygons to well-developed crystals.

4.4 Summary and conclusions

Previous experimental results from batch cementation tests led to the conclusion that copper and antimony form a substrate on zinc dust. This substrate enhances the reduction rate of cobalt. In this research, an electrolytic cell was used to test the properties of copper and antimony as a substrate for the reduction of cobalt, taking into consideration the compositional analysis and morphology of the deposit, growth mechanism and the relation between current density and potential. The effect of common process parameters on the deposition of cobalt was also examined. The conclusions reached are as follows:

In the presence of zinc, cobalt always codeposits with zinc as a cobalt-zinc alloy. Under virtually all conditions, underdeposited zinc is the major constituent of the deposit. The cobalt content of the cobalt-zinc alloy on an antimony substrate is ten times higher than on a copper substrate. A suggested explanation for the affinity of cobalt to deposit on antimony may be a lower surface energy barrier between these two metals. This facilitates the formation of a nucleus of a cobalt-zinc alloy with an increased cobalt content, which forms the base for further growth. In subsequent stages of the development of the crystal, the increased cobalt content of the alloy is maintained.

At a low cobalt content of the cobalt-zinc deposit, the morphology is polygonal, whereas the deposit becomes nodular at a high cobalt level. This is caused by internal stresses in the deposit which is caused through the lattice mismatch between cobalt and zinc. This effect becomes more pronounced as the cobalt content increases. The nodular morphology of the cobalt deposits was the same as that obtained from cobalt cementation with zinc dust using copper-antimony activation.

Factors which increase the cobalt content of the alloy are a low current density and a high temperature. The cobalt content of the deposit is highly inhibited by the presence of organics, although the deposition of zinc remains unaffected. No changes in alloy composition occur by the variation of the bulk solution pH, even beyond the stage where basic zinc sulphate is formed.

5 ELECTROCHEMICAL COBALT REMOVAL: KINETIC ASPECTS

5.1 Introduction

Batch cementation tests led to the conclusion that copper and antimony form a preferential substrate on zinc dust which enhances the reduction rate of cobalt. To examine their properties in enhancing cobalt reduction, copper and antimony were tested as cathode substrates in an electrochemical cell. The objective of this research was to determine the kinetics of cobalt deposition from a zinc electrolyte to further determine the mechanism and supplement it with kinetic data. The experimental apparatus was in the form of an electrochemical cell, similar to the one used before but with a higher ratio of cathode surface area to solution volume. The purpose of this cell was to measure cobalt removal rates from solution as a function of different parameters. The parameters which were tested were the influence of substrate, antimony addition, current density, temperature, pH and organics.

5.2 Experimental details

Electrolysis cell

The electrolytic cell consisted of a 300-mL glass beaker fitted with a slotted Plexiglas lid (Figure 5.1). The distance between the anode and the cathode was 3 cm. The platinum wire anode was placed in a glass fritted disc to prevent the evolving oxygen from diffusing into the electrolyte and subsequently contacting the cathode. Nitrogen sparging of the solution was started 15 minutes before the beginning of each experiment and continued throughout the experiment in order to eliminate traces of dissolved oxygen. 275 mL of solution was used for each experiment. The temperature was controlled by a constant temperature water bath at 73 ± 1 °C, unless otherwise stated. A marine type impeller with a diameter of 50 mm provided agitation at a rotation speed of 300 rpm. A Hokuto Denko galvanostat/potentiostat model HA-211 A supplied the power for the cell.

Figure 5.1: Electrochemical cell

Cathodes

Copper and antimony were used as cathode substrates. The copper electrode was cut from a 1-mm thick commercial grade copper sheet. Microstop was used as a masking paint to mask the cathode surface area to a surface area of 30 cm² (6 x 5 cm). An insulated electrical wire was soldered at the back of the sheet to provide electrical contact. The antimony substrate was prepared by plating antimony from a 0.2 M antimony tartrate solution onto a copper cathode at 75-100 A/m² for at least 45 minutes. This produced an antimony layer with a thickness of several microns. Before each experiment, the copper cathodes were cleaned with 20 % nitric acid to remove the film of oxidized copper and then rinsed with distilled water. The antimony cathodes were rinsed with distilled water only.

Electrolyte

The electrolyte used was a purified zinc solution from Cominco Ltd.. It was treated with activated carbon to remove organics and cemented with zinc dust to remove any traces of cobalt, copper and antimony. The zinc content was 155 g/L and the pH was 4.0 (at 73 °C). The electrolyte was spiked with 30 ppm cobalt from an aqueous stock solution of cobalt sulphate ($\text{CoSO}_4 \cdot 5\text{H}_2\text{O}$). When antimony was used in solution, it was added from an aqueous antimony tartrate stock solution ($\text{K}(\text{SbO})\text{C}_4\text{H}_6\text{O}_6 \cdot 0.5\text{H}_2\text{O}$).

5.2.1 Experiments

The influence of current density, substrate, pH, antimony addition, organics and temperature on cobalt removal was determined using the following base line conditions: antimony substrate, 30 A/m^2 , 73 °C, initial pH 4.0, no organics or antimony in solution. The solution was plated for 180 minutes at constant current density. Duplicate 2-ml samples of the electrolyte were taken at 30, 60, 120 and 180 minutes from the beginning of the experiment. The samples were analyzed for cobalt by a colorimetric method using nitroso-R salt. At the end of the experiment, the cathode was immediately removed from solution and thoroughly rinsed with distilled water.

5.3 Results and discussion

5.3.1 Effect of substrate

In this experiment, copper and antimony substrates were used for the removal of cobalt from zinc electrolyte. The antimony cathode was plated at various current densities in the range 20 to 50 A/m^2 and the copper cathode was plated at 30 A/m^2 . The objective was to study the properties of these two metals as preferential substrates for the removal of cobalt. Secondly, the effect of current density on cobalt removal was studied. Figure 5.2 shows the cobalt deposition kinetics on the copper and antimony substrates, which are presented by the dotted and the full lines respectively. Similar to cementation, cobalt removal follows first-order kinetics. The cobalt removal rates are ten times higher on antimony than on copper. As shown in the previous

chapter, the cobalt content of the electrodeposited cobalt-zinc alloy is much higher on antimony than on copper. Subsequently, the higher cobalt content on antimony results in higher cobalt removal kinetics than on copper. Clearly, antimony enhances cobalt removal by exhibiting properties which increase the cobalt content of the deposit and thus its removal rate, unlike copper.

Figure 5.2: Cobalt removal as a function of substrate and current density. 30 ppm Co, 73 °C, initial pH 4.0, antimony substrate: full lines, copper substrate: dotted line.

5.3.2 Effect of antimony addition

In the previous chapter it was shown that the cobalt content of the deposit on copper was increased by the addition of antimony to the solution. It was therefore assumed that antimony forms nucleation sites for a cobalt-rich cobalt-zinc alloy. To prove this, a copper substrate was used and various concentrations of antimony were added to the solution.

Figure 5.3 shows the removal of cobalt on a copper substrate as 0 to 10 ppm antimony is added to the solution. Up to 3 ppm, the kinetics of cobalt removal are significantly improved with increasing antimony addition. Beyond this concentration, more antimony does not result in any significant additional cobalt removal. Figure 5.4 represents a plot of the kinetic rate of cobalt removal as a function of the antimony concentration. It shows clearly two regions: a steep curve

in the beginning represents a fast increase in cobalt removal with increasing antimony additions. Beyond a concentration of 3 ppm, the curve flattens out indicating that more antimony does not enhance cobalt removal any further.

Figure 5.3: Cobalt removal on copper substrate as a function of antimony addition. 30 ppm Co, 73 °C, 30 A/m².

Figure 5.5 compares the cobalt deposition rates on copper, an antimony substrate and a copper substrate with 3 ppm antimony added to solution. The rates are the same for the latter two experiments. This can be explained with the proposed theory that antimony provides nucleation sites. With increasing antimony addition, more sites are available for the deposition of a cobalt-rich cobalt-zinc alloy and cobalt removal increases subsequently. When a certain number of nucleation sites is achieved, cobalt removal does not increase further. The reason for this is that at this point the rate of cobalt deposition is limited by other factors, in particular its thermodynamic driving force.

Figure 5.4: Cobalt removal rate on copper substrate as a function of antimony addition. 30 ppm Co, 73 °C, 30 A/m².

Figure 5.5: Cobalt removal on antimony and copper substrate with and without antimony added to solution. 30 ppm Co, 73 °C, 30 A/m², initial pH 4.0

5.3.3 Effect of temperature

In this experiment, the effect of temperature on the removal of cobalt was studied.

Figure 5.6 shows the cobalt removal rates at various temperatures. By increasing the temperature from 50 to 85 °C, a higher removal rate is obtained. However, at 90 °C, the cobalt removal rate drops considerably. This is contradictory with the elevated cobalt content of the deposit and the fast cobalt removal rates obtained in cementation [12,17,33], which predict increased cobalt removal rate beyond 85 °C. The explanation can be found in Table 5.1, which shows an estimate of the current distribution between the cathodic reactions of cobalt and zinc deposition and the parasitic hydrogen evolution reaction at 85 and 90 °C. The relative distribution was calculated with the experimentally found cobalt removal rate and the composition of the cathode deposit, obtained from SEM analysis. At 85 °C, 50 % of the total cathodic current is used for the reduction of cobalt and zinc to metal and the rest of the current is consumed by hydrogen evolution. Upon increasing the temperature to 90 °C, hydrogen evolution becomes the most prominent reaction. Only 2 % of the cathodic current is used for metal deposition, the remaining current being used for the evolution of hydrogen.

The increase in hydrogen evolution is most likely caused by the change in deposit composition. At temperatures up to 85 °C, the main constituent of the deposited cobalt-zinc alloy is zinc. The cathode properties for hydrogen evolution are thus primarily governed by zinc, which is known for its high hydrogen evolution overpotential. At 90 °C, the major part of the deposit consists of cobalt, which highly catalyzes the evolution of hydrogen. Consequently, the catalyzed hydrogen evolution reaction becomes more favorable than metal deposition.

Cobalt removal by zinc dust cementation increases with increasing temperature and does not drop after a certain temperature. This can be explained by the fact that the potential difference in cementation is constant which means that the current density is not fixed but depends on the reactions taking place. At higher temperatures hydrogen evolution becomes relatively the highest consumer of cathodic current. Consequently, cobalt removal can only increase when the total cathodic current increases. When zinc dust is used to remove cobalt from solution, a higher zinc dust consumption can be expected with increasing the temperature due to the increased hydrogen evolution.

Figure 5.6: Cobalt removal on antimony substrate as a function of temperature. 30 ppm Co, 30 A/m², initial pH 4.0.

Table 5.1: Cobalt removal, deposit composition and estimated cathodic current distribution on antimony substrate as a function of temperature. 30 ppm Co, 30 A/m², initial pH 4.0

Temperature (°C)	k_{Co} (m/s)	Co in deposit (wt.%)	Zn in deposit (wt.%)	i_{Co} (%)	i_{Zn} (%)	i_{H_2} (%)
85	$10.3 \cdot 10^{-5}$	7	93	3.5	46.5	50
90	$4.4 \cdot 10^{-5}$	76	24	1.5	0.5	98

The Arrhenius plot for cobalt deposition in the temperature range of 50 to 85 °C (Figure 5.7) gives an activation energy of 65 kJ/mole, which is typical for a process under chemical or electrochemical control.

Figure 5.7: Arrhenius plot of cobalt removal on antimony substrate. 30 ppm Co, 30 A/m², initial pH 4.0.

5.3.4 Effect of pH

In this experiment, the influence of acidity on the removal of cobalt and hydrogen evolution was studied at an initial pH value of 4.0 which was not adjusted and at three constant pH values viz, 1.5, 4.0 and 4.6.

In the experimental cell, the pH changes due to the anodic and cathodic reactions which involve hydrogen. Hydrogen ions are released at the anode from the oxidation of water. At the cathode, hydrogen gas is generated from the reduction of hydrogen ions. When in addition, a metal is deposited at the cathode, more acid is released than consumed, causing a decrease of solution pH. To investigate the effect of constant pH, the electrolyte pH has to be adjusted continuously. A pH buffer was not used, because the addition of foreign species may change the cathode reactions by their adsorption onto the electrode. A commonly used buffer in cobalt-zinc plating is boric acid. The boric acid adsorbs onto active sites of the cathode surface, blocking the surface selectively for cobalt deposition, which results in a cobalt-zinc alloy with a lowered cobalt content [48].

basic zinc compounds and some zinc oxide in solution buffered the pH throughout the experiment. The acidity of the pH 4.0 solution was maintained constant by a pH controller by the addition of a concentrated sodium hydroxide solution. The pH 1.5 solution was adjusted to its initial pH value with sulphuric acid. Due to its high concentration of hydrogen ions, the pH did not change during the experiment.

Figure 5.8 shows the cobalt removal rate as a function of pH. The worst cobalt removal is obtained at the lowest pH. Because cobalt reduction and hydrogen evolution are competing reactions, the increased supply of hydrogen ions at the cathode, increases hydrogen evolution at the expense of metal deposition. Consequently, better cobalt removal is obtained at a higher pH. However, it has been stated that above a limiting pH, the formation of basic zinc sulphate inhibits cobalt deposition [15,16]. This is not in agreement with the obtained rates, which show that cobalt removal increases with increasing pH, also beyond the point at which basic zinc sulphate is formed. Thus it can be concluded that a low pH is more detrimental to the cobalt deposition rate than a high pH, which has also been found in zinc dust cementation [33].

Figure 5.8: Cobalt removal on antimony substrate as a function of pH. 30 ppm Co, 73 °C, 30 A/m².

5.3.5 Effect of organics

This experiment deals with the effect of organics on the electrolytic removal of cobalt.

Figure 5.9 shows the effect of organics in the electrolyte on cobalt removal. Compared to the organic-free solution, cobalt deposition is greatly reduced in the presence of organics. Organics in the form of 3 ppm Percol 338, reduce the cobalt removal rate by approximately 70 %. As shown in the previous chapter, organics inhibit cobalt deposition, but do not affect zinc reduction. Inhibition by the presence of organics can have two causes. Firstly, organics can complex with cobalt to form a compound which reduction on the cathode is more difficult than that of uncomplexed cobalt. Secondly, organics can adsorb onto the cathode surface, blocking active cathode sites for cobalt reduction. It is most likely that the reduced cobalt removal rate is caused by the adsorption effect because the ratio of organic:cobalt is too low to result in a large complexation degree. It can be concluded that for cobalt removal the organic content of the electrolyte has to be controlled at a level as low as possible.

Figure 5.9: Cobalt removal on antimony substrate in the presence of organics. 30 ppm Co, 73 °C, 30 A/m², initial pH 4.0, organic: 3 ppm Percol 338.

5.3.6 X-ray diffraction analysis

Several electrodeposits were subjected to X-ray diffraction analysis to identify the phases in the deposited cobalt-zinc compound. The electrodeposits studied were three antimony cathodes, plated at 73, 85 and 90 °C and a copper cathode deposited at 73 °C, without the addition of antimony to solution. Due to the small quantity of cathode deposits, it was decided not to remove the deposit but to use the plated electrode. Copper and antimony electrodes without deposit were used as blanks. The X-ray diffraction analysis was carried out with a Siemens D 5000 diffractometer. The samples were run from 3 to 60° (2 θ) in steps of 0.02 (2 θ) at a scan rate of 0.8 second per step. No peaks were found under 20°. Figure 5.10 shows the diffraction pattern of the electrodeposited copper cathode. Clearly, only electrodeposited zinc and copper from the underlying cathode substrate can be distinguished. Due to the very small amount of cobalt in the deposit, it could not be identified. No deposit could be identified on the antimony cathode deposited at 90 °C, because the deposit was either amorphous or too thin. Figures 5.11 and 5.12 show the diffraction patterns on the antimony cathodes at 73 and 85 °C respectively. In both samples, three elemental metal phases could be identified, namely copper and antimony from the cathode substrate and a large amount of zinc in the form of an electrodeposit. No pure cobalt or known cobalt-zinc compounds were found. However, both diffractograms contain a peak at approximately 42.5° just before the main zinc peak, which could not be identified. Because the cobalt levels of the cobalt-zinc deposits are well within the limits of detection of the XRD, this peak must correspond to a cobalt-containing compound, which might be a cobalt-zinc intermetallic. This is further confirmed by the height of the peak. At 85 °C, the peak is larger than at 73 °C because of the higher cobalt content of the deposit at the increased temperature. It can be concluded that the electrodeposited cobalt-zinc alloy consists of a solid solution of underpotentially deposited zinc and a cobalt-containing compound which might be a cobalt-zinc intermetallic.

Figure 5.10: XRD pattern of cobalt-zinc alloy deposited on copper substrate at 73 °C. 30 ppm Co, 30 A/m², initial pH 4.0.

Figure 5.11: XRD pattern of cobalt-zinc alloy deposited on antimony substrate at 73 °C. 30 ppm Co, 30 A/m², initial pH 4.0.

Figure 5.12: XRD pattern of cobalt-zinc alloy on antimony substrate deposited at 85 °C. 30 ppm Co, 30 A/m², initial pH 4.0.

5.4 Summary and conclusions

An electrochemical cell was used to determine the kinetics of electrolytic cobalt removal from zinc electrolyte. The objective was to study the influence of various process parameters on cobalt removal and to further elucidate the mechanism by which copper and antimony enhance cobalt deposition. The following conclusions were reached:

The removal of cobalt is ten times higher on antimony than on copper substrates.

The cobalt deposition on copper can be improved significantly by the addition of small concentrations of antimony. The improvement levels off after a certain concentration at which cobalt removal becomes the same as on a pure antimony substrate. It was confirmed that antimony enhances cobalt removal by acting as a preferential substrate for the formation of cobalt-zinc alloys with an increased cobalt content. Such a property could not be assigned to copper substrates. The deposited cobalt-zinc alloy was identified by X-ray diffraction as a solid solution of zinc and a cobalt compound which does not consist of a pure cobalt, but is most likely a cobalt containing compound such as a cobalt-zinc intermetallic.

Higher temperatures increase the cobalt content of the cobalt-zinc deposit and consequently the cobalt kinetics. However, above a certain temperature, the hydrogen evolution becomes the predominant reaction, which is may be partly caused by the high cobalt content of the deposit. Cobalt deposition is a chemically or electrochemically controlled process with an activation energy of 65 kJ/mole.

With increasing solution pH, cobalt removal is increased due to a lowered discharge of hydrogen evolution. The formation of basic zinc sulphates at a higher solution pH does not inhibit cobalt deposition. The presence of organics in the electrolyte reduces the kinetics of cobalt removal considerably.

6 GENERAL SUMMARY AND CONCLUSIONS

This study has been concerned with the identification of the mechanism of copper-antimony activated cementation of cobalt by zinc dust from zinc electrolyte. Secondly, the effect of common process parameters on cobalt cementation has been investigated. Both reaction kinetics and electrochemical investigations of the reduction of cobalt were used to determine these aspects. On the basis of the results from the various experimental techniques, the following conclusions were drawn:

Mechanism

Cobalt always codeposits as a cobalt-zinc alloy when it is reduced from a zinc electrolyte. This alloy predominantly consists of underdeposited zinc. It is therefore difficult to remove cobalt from zinc electrolyte by means of cementation with zinc dust. The addition of copper and antimony improve cobalt cementation in the following way: copper and antimony cement out of solution in the early stages of the cementation process, forming a preferential substrate for cobalt deposition. Copper deposits as a highly dendritic precipitate, thereby markedly increasing the cathodic surface area of the zinc dust. Antimony forms numerous small cathodic sites on the dust surface, onto which the cobalt-zinc alloy with an increased cobalt content can nucleate. Once these nuclei are formed, they can continue growing while their high cobalt content is maintained. The affinity of cobalt to deposit onto antimony may be a lowered surface energy barrier between these two metals, which enhances the deposition of cobalt in the cobalt-zinc alloy. This cobalt-zinc alloy consists of a solid solution of underdeposited zinc and a cobalt containing compound, which is possibly a cobalt-zinc intermetallic. Cobalt deposition was found to be under chemical or electrochemical control with an activation energy of 65 kJ/mole.

Effect of temperature

Because cobalt cementation is under chemical control, higher temperatures increase the kinetics of cobalt removal considerably. However, the competing reaction of hydrogen evolution may also become severe, leading to a high consumption of zinc dust. With increasing temperature, the cobalt content of the cobalt-zinc alloy increases exponentially. The morphology of the cobalt-zinc deposit is determined by its composition. With increasing cobalt content, i.e. increasing temperature, the morphology changes from a polygonal to a nodular shape and finally to a smooth deposit. The increased cobalt content causes internal stresses in the deposit due to lattice mismatch between cobalt and zinc, which leads to the formation of nodules rather than well-defined crystals. When cobalt is the prime constituent of the alloy, it dominates the morphology characteristics, resulting in a smooth deposit.

Effect of pH

The composition of the cobalt-zinc alloy remains unchanged at different values of solution pH. The kinetics of cobalt deposition are affected by the presence of free acid which is competing with cobalt and zinc ions for reduction at the cathodic sites. As the solution pH is increased, the lowered supply of hydrogen ions at the cathode decreases hydrogen evolution, favoring cobalt removal. Increasing the pH beyond the stage where precipitates of basic zinc compounds form does not result in the inhibition of cobalt deposition.

Effect of organics

The presence of organics in the electrolyte has a highly adverse effect on cobalt deposition. The adsorption of the organic compound on the cathodic sites inhibits cobalt depositions, which leads to a lowered cobalt content in the cobalt-zinc alloy. Consequently, the kinetics of cobalt removal are decreased when organics are present in the electrolyte.

7 INDUSTRIAL SIGNIFICANCE

This research has been concerned with the fundamental aspects of cobalt cementation in the presence of copper and antimony in order to provide a better understanding of the mechanism. It was not the objective to provide a revised technology which can be implemented directly in the existing process. The general recommendations follow the existing knowledge which has been developed in practice: high temperature, high pH, no organics in the electrolyte and a large zinc dust area benefit cobalt removal most. The presence of organics in the electrolyte imposes the most detrimental effect on cobalt removal. It is therefore most important to keep the level of organics as low as possible.

At first glance, cobalt cementation with zinc dust may seem to be a costly and inefficient method because the consumption of zinc dust is very high compared to the amount of cobalt removed. However, it is a simple and reliable method as long as the operating conditions are run optimally. Cobalt removal by means of an electrochemical cell is not likely to be a feasible alternative to cementation for the following reasons:

Firstly, cobalt removal in an electrochemical cell is as sensitive to poor operating conditions as is zinc dust cementation in the plant. In other words, an electrochemical cell will not prevent cobalt breakthrough when, for example, the organics in the electrolyte are high.

Secondly, the parasitic hydrogen evolution makes electrowinning a process with reduced current efficiency, especially at high temperatures. Cementation is a potentiostatic process which can benefit by operating cobalt cementation at high temperatures where both cobalt deposition and hydrogen evolution increase without a higher addition for zinc dust.

Thirdly, with fluctuating cobalt levels or other reasons which demand increased removal means, the addition of more or finer dust makes cementation a more flexible option.

Finally, it is doubtful whether the electrowinning of cobalt is a more economic option considering the necessary equipment and most importantly the high energy consumption in the process.

8 RECOMMENDATIONS

This research has shown that in the presence of zinc, cobalt codeposits anomalously with zinc as an alloy. Most of this alloy consists of the underdeposited zinc, which is the reason for the poor removal of cobalt by zinc cementation in the absence of activating species. Antimony acts as a substrate onto which cobalt-zinc nuclei with an increased cobalt content can deposit and further develop to crystals while maintaining their high cobalt content.

Further studies should focus on the mechanism of the anomalous deposition of cobalt with zinc. Although it is well known that all iron group metals show such behavior, there is controversy on the mechanism of the deposition and little supporting evidence for the proposed theories. Another area of study is the influence of the substrate in modifying the anomalous deposition behavior. Such a study should address two questions. Firstly, why is antimony as a substrate able to enhance cobalt deposition. Secondly, why is the high cobalt content of the cobalt-zinc alloy maintained during further growth after the antimony substrate is deposited with thousands of monolayers.

Another area of cobalt electrochemistry of interest lies in the electrowinning of zinc. It is known that relatively very high cobalt levels can be tolerated in the tankhouse, without lowering the quality of zinc or the current efficiency. However, this is only possible when certain other impurities, which in combination with cobalt detrimentally affect zinc electrowinning are absent. A combination of cobalt and antimony is one of the worst for zinc electrowinning. It lowers the current efficiency and so-called active centers form which create holes in the zinc cathode. This localized corrosion has much in common with the antimony activated deposition of cobalt which takes place locally on active antimony sites and accompanies hydrogen evolution. It would be of interest to investigate the similarities between the cobalt cementation and the mechanism of cobalt interference in electrowinning. A subsequent stage should deal with the prevention of the synergistic effect. This would most likely be in the form of the addition of organics. However, these organics should be rapidly degradable and do not inhibit cobalt cementation when the solution is recycled. Alternately, the organics should be adsorbed in the hydrolytic precipitation of iron.

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APPENDIX A: SEM PHOTOGRAPHS

Figure p-3.1a: Zinc dust before cementation. Magnification 200 x.

Figure p-3.1b: Zinc dust before cementation. Magnification 2,000 x.

Figure p-3.2a: Zinc dust after cementation of copper and antimony. Magnification 200 x. Conditions: 30 ppm Cu, 1.5 ppm Sb, 73 °C, initial pH 3.6, 120 minutes.

Figure p-3.2b: Zinc dust after cementation of copper and antimony. Magnification 2,000 x. Conditions: 30 ppm Cu, 1.5 ppm Sb, 73 °C, initial pH 3.6, 120 minutes.

Figure p-3.3a: Copper-antimony pre-cemented zinc dust after cementation of cobalt. Magnification 200 x. Conditions: 30 ppm Co, 73 °C, initial pH 3.6, 120 minutes.

Figure p-3.3b: Copper-antimony pre-cemented zinc dust after cementation of cobalt. Magnification 2,000 x. Conditions: 30 ppm Co, 73 °C, initial pH 3.6, 120 minutes.

Figure p-3.4 a: Cross-section of copper-antimony pre-cemented zinc dust after cementation of cobalt. Magnification 200 x. Conditions: 30 ppm Cu, 1.5 ppm Sb, ppm Co, 73 °C, initial pH 3.6, 120 minutes.

Figure p-3.4 b: Cross-section of copper-antimony pre-cemented zinc dust after cementation of cobalt. Magnification 2,000 x. Conditions: 30 ppm Cu, 1.5 ppm Sb, ppm Co, 73 °C, initial pH 3.6, 120 minutes.

Figure p-4.1: Morphology of cobalt-zinc deposit on copper substrate.
Magnification: 2,000 x. Conditions: 30 ppm Co, 30 A/m², 73 °C, pH 3.0

Figure p-4.2: Morphology of cobalt-zinc deposit on antimony substrate, nodular type.
Magnification: 700 x. Conditions: 30 ppm Co, 20 A/m², 73 °C, pH 3.0.

Figure p-4.3: Morphology of cobalt-zinc deposit on antimony substrate, polygonal type. Magnification: 1,200 x. Conditions: 30 ppm Co, 40 A/m², 73 °C, pH 3.0

Figure p-4.4: Morphology of cobalt-zinc deposit on antimony substrate, combined polygonal-nodular type. Magnification: 1,500 x. Conditions: 30 ppm Co, 50 A/m², 73 °C, pH 3.0

Figure p-4.5: Different morphology types of cobalt-zinc deposits on antimony substrate. Magnification: 200 x. Conditions: 30 ppm Co, 50 A/m², 73 °C, pH 3.0

Figure p-4.6: Cross-section of polygonal cobalt-zinc deposit on antimony substrate. Magnification: 1,700 x. Conditions: 30 ppm Co, 30 A/m², 50 °C, pH 3.0.

Figure p-4.7a: Cross-section of nodular cobalt-zinc deposit on antimony substrate. Magnification: 1,700 x. Conditions: 30 ppm Co, 30 A/m², 85 °C, pH 3.0.

Figure p-4.7b: Cobalt X-ray dot map of cross-section of nodular cobalt-zinc deposit on antimony substrate. Cross-section shown in figure p-4.7a.

Figure p-4.7b: Zinc X-ray dot map of cross-section of nodular cobalt-zinc deposit on antimony substrate. Cross-section shown in figure p-4.7a.

APPENDIX B: EH-PH DIAGRAM FOR THE SYSTEM Zn-SO₄-H₂O

The Eh-pH diagram of the zinc-sulphate-water system are shown with and without the formation of basic zinc sulphate at 73 °C and 155 g/L zinc. The thermodynamic data of entropy and heat capacity for basic zinc sulphate were derived from Fountoulakis [15] who calculated these with the Latimer's method. The other thermodynamic data were taken from the NBS handbook [49].

Eh-pH diagram for 155 g/L zinc at 73 °C without the formation of basic zinc sulphate compounds.

Eh-pH diagram for 155 g/L zinc at 73 °C with the formation of basic zinc sulphate compounds.

APPENDIX C: CALCULATION OF ELECTROCHEMICAL POTENTIALS

Higher temperatures affect the free energy of species and subsequently their electrochemical potentials. The free energy change can be corrected with the following formula:

$$\Delta G_{T_2}^{\circ} = \Delta G_{T_1}^{\circ} + \Delta T * \Delta |\overline{C_p}|_{T_1}^{T_2} - \Delta T * \Delta (S_{T_1}^{\circ})_{\text{abs}} - T_2 * \Delta |\overline{C_p}|_{T_1}^{T_2} \ln \left(\frac{T_2}{T_1} \right)$$

in which $|\overline{C_p}|_{T_1}^{T_2}$ is the average heat capacity of a species between T_1 and T_2

By convention:

$$T_1 = 298 \text{ K}$$

$$T_2 = T \text{ (here 346 K)}$$

$$\Delta G_T^{\circ} = \Delta G_{298}^{\circ} + \Delta T * \Delta |\overline{C_p}|_{298}^T - \Delta T * \Delta (S_{298}^{\circ})_{\text{abs}} - T * \Delta |\overline{C_p}|_{298}^T \ln \frac{T}{298}$$

$$(S_{298}^{\circ})_{\text{abs}} = (S_{298}^{\circ})_{\text{conv}} - 5.0 (z)$$

$$\Delta T = T - 298$$

Heat capacity calculation for ionic species (Criss and Coble):

$$|\overline{C_p}|_{298}^T = \alpha_T + \beta_T (S_{298}^{\circ})_{\text{abs}}$$

$$\alpha_T = \frac{a_T}{\ln \left(\frac{T}{298} \right)}$$

$$\beta_T = \frac{(1.0 - b_T)}{\ln \left(\frac{T}{298} \right)}$$

The entropy constants for simple cations at various temperatures are given by [51]:

T (°C)	a _T (cal/mol)	b _T (cal/mol)
25	0	1.000
60	3.9	0.955
100	10.3	0.876
150	16.2	0.792

Constants for intermediate temperatures are derived by linear interpolation. At 73 °C the constants were found to be a_T= 6.176 and b_T= 0.924, resulting in α_T= 41.354 and β_T = -0.509.

Heat capacity calculation for elements:

$$C_p = a + (b * 10^{-3})T + (c * 10^{-6})T^2 + \frac{d * 10^5}{T^2}$$

$$|\overline{C}_p|_{298}^T = \frac{1}{\Delta T} a * T + \frac{1}{2}(b * 10^{-3})T^2 + \frac{1}{3}(c * 10^{-6})T^3 - \frac{d * 10^5}{T} \Big|_{298}^T$$

Heat capacity of water:

$$|\overline{C}_p|_{298}^T = 18.0 \text{ cal/mol} \cdot \text{K}$$

Free energy data of the species:

species	ΔG° ₂₉₈	(S° ₂₉₈) _{conv}	z	a	b	c	d	(S° ₂₉₈) _{abs}	\overline{C}_p ₂₉₈ ³⁴⁶
	(cal/mol)	(cal/mol)		(cal/mol)	(cal/mol)	(cal/mol)	(cal/mol)	(cal/mol)	(cal/mol)
SbO ⁺	-42019	5.34	1					0.34	41.2
H ⁺	0	0	1					-5	105.2
Cu ²⁺	15550	-23.25	2					-33.25	670
Zn ²⁺	-35205	-25.72	2					-35.72	752
Co ²⁺	-13000	-27.0	2					-37.0	779
H ₂ O	-56741	16.72	0					16.72	6.9
H ₂ (g)	0	31.26	0	6.62	0.81	-	-	31.26	18.0
Co	0	6.8	0	4.72	4.3	-	-	6.8	6.1
Zn	0	9.95	0	5.35	2.4	-	-	9.95	6.1
Cu	0	7.97	0	5.41	1.5	-	-	7.97	5.9
Sb	0	10.5	0	5.51	1.74	-	-	10.5	6.1

The electrochemical potentials under standard and experimental conditions become:

reaction	$\Delta(S_{298}^{\circ})_{\text{abs}}$	$\Delta \overline{C}_p _{298}^{346}$	ΔG_{298}°	ΔG_{346}°	E_{298}°	E_{346}°	E_{346}
	(cal/mol)	(cal/mol*K)	(cal/mol)	(cal/mol)	mV	mV	mV
$\text{SbO}^+ + 2\text{H}^+ + 3\text{e} \rightarrow \text{Sb} + \text{H}_2\text{O}$	36.88	-228	-14722	-15656	213	226	-22
$\text{Cu}^{2+} + 2\text{e} \rightarrow \text{Cu}$	41.22	-694	-15550	-14980	337	324	210
$\text{Zn}^{2+} + 2\text{e} \rightarrow \text{Zn}$	45.67	-746	35205	35726	-762	-774	-761
$2\text{H}^+ \rightarrow \text{H}_2(\text{g})$	41.26	-204	0	-1233	0	27	-248
$\text{Co}^{2+} \rightarrow \text{Co}$	43.8	-773	13000	13736	-282	-297	-411

Experimental conditions: 155 g/L Zn, 30 ppm Cu, 30 ppm Co, 1.5 ppm Sb and pH 4.0 at 73 °C.

APPENDIX D: PROCEDURE FOR COLORIMETRIC COBALT ANALYSIS

The colorimetric cobalt analysis is based on the complexation of cobalt with the organic salt Nitroso-R-salt ($\text{C}_{10}\text{H}_4(\text{OH})(\text{SO}_3\text{Na})_2\text{NO}$). Cobalt and Nitroso-R form a soluble coloured cobalt complex, which intensity was measured colorimetrically with a Bausch and Lomb Specronic 20. By comparing the measured intensity with those of known standards, the cobalt concentration was determined.

Colorimetric method:

- Pipet 2 mL of sample into a clean, dry 100 mL flask
- Add 20 mL of distilled water
- Add 5 mL of Nitroso-R-salt solution
- Boil 1-2 minutes
- Add 1 mL potassium bromate solution to oxidize and destroy uncomplexed nitroso-R
- Boil 1 minute
- Add 1 mL of concentrated nitric acid to destroy organic complexes other than cobalt
- Cool solution
- Transfer solution into sample cuvet
- Measure intensity of the colour with colorimeter at 520 nm wavelength
- Compare intensity with intensity of standard solutions

Preparation of standards:

Standards and Nitroso-R-salt solution were made up every day, because the colour of nitroso-R deteriorates with time.

Nitroso-R solution: 0.5 wt. %

Dissolve 0.5 g salt in 100 mL distilled water.

Potassium Bromate solution: 3 wt.%

Dissolve 3.0 g salt in 100 mL distilled water.

Blank

Distilled water.

Standards

5, 15 and 30 ppm cobalt as cobalt sulphate in zinc electrolyte. The standards were prepared in the same manner as the sample. The relationship between the intensity of the standards and the concentration was linear and consistent. Therefore, it was decided to only use a blank and a sample of the solution which was used in the experiments containing 30 ppm cobalt.