

國立交通大學

材料科學與工程研究所

碩士論文

利用銦-錫氧化物(ITO)廢料回收高純度銦材
Recycling high purity indium from ITO wasted
materials

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中華民國九十七年七月

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碩士論文

A Thesis

Submitted to Department of Material Science and Engineering

College of Engineering

National Chiao Tung University

in partial Fulfillment of the Requirements

for the Degree of

Master

in

Materials Science & Engineering

July 2008

Hsinchu, Taiwan, Republic of China

中華民國九十七年七月

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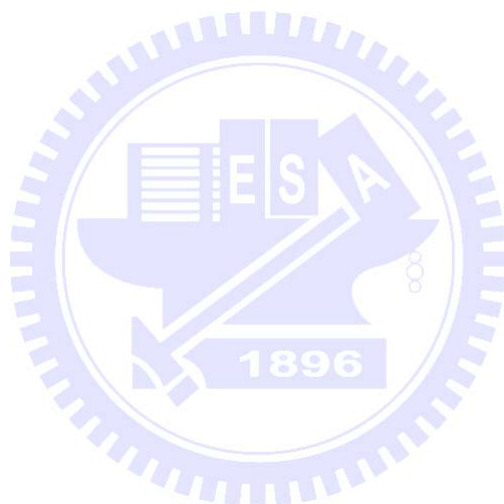
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摘要

內含銦-錫氧化物的 ITO 酸洗液或 ITO 汙泥中含有貴金屬銦，本研究將整合濕法冶金與火法冶金，提供一具經濟價值之銦回收方法。銦於溶液中為離子狀態，利用濕法冶金法(電析法或化學置換法)可將銦元素由溶液中取出，另外火法冶金法(造渣技術)可將銦元素由固態廢料中取出，以上所得的粗銦經真空熔煉後可使金屬銦與氧化層分離，可得到 3N(99.9%)高純度之銦材。回收後的銦材由感應耦合電漿質譜儀、分析掃描式電子顯微鏡、能量分散光譜儀、光學顯微鏡分析，從銦的顯微組織、成份分析之結果，銦的純度可達到 3N。回收 ITO 酸洗液可以得到純銦 17.69g/L，且其純度為 3N。回收酸洗液的過程中，以鎂粉當做濕法冶金中的置換劑，其鎂粉的量約為 4.67g/L，且操作溫度在室溫下便可。另外氫氧化鈉為火法冶金中的造渣物質，添加量大約 6g/L 可以得到 17.69g/L 的純銦。回收 ITO 汙泥可以得到 5.39g/L 的純銦，且其純度為 99.7%。在回收汙泥的過程中，以鋅粉作為濕法冶金中的置換劑，其鋅粉的量約為 3g/L，且操作溫度需超過攝氏 60 度才會反應完全。氫氧化鉀為火法冶金中的造渣物質，添加量

大約 5.33g/L 可以得到 5.39g/L 的純鈰。從濕法冶金中若可置換出越多的海綿鈰，則在火法冶金中獲得的鈰含量也相對提高一些。在本實驗中，從酸洗廢液置換出的海綿鈰，經火法冶金提煉後鈰的損失率為 33%，由污泥廢料中提煉出的純鈰其損失率為 24%。

本研究針對鈰元素的回收方法、回收效率，結合濕法冶金及火法冶金法，製作出高純度的鈰材。另外，本研究亦將藉由此題目，深入探討鈰之電化學與熱力學反應特性。



Recycling high purity indium from ITO wasted materials

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Abstract

The study was used to establish a method to recycle indium from ITO wasted solution and ITO wasted mud. The economical and efficient method was presented in the processes of hydrometallurgy and pyrometallurgy. In the hydrometallurgy method (chemical replacement), the powder of Mg and Zn were used to be the reducing agents. No matter in the ITO wasted solution or ITO wasted mud, the sponge indium was obtained by hydrometallurgy. In the pyrometallurgy method (slags making), the alkali compounds liked NaOH and KOH were used to make slags. The pure indium with a purity of 99.9% (3N) could be obtained from the sponge indium. The recycled indium was analyzed by Scanning Electron Microscopy, Energy Dispersive X-ray analysis, Inductively Coupled Plasma-mass spectrometry and Optical Microscope. In recycling indium from ITO wasted solution, the addition of Mg was 4.67g/L to replace the sponge indium and the operation temperature was room temperature. Moreover, the addition of NaOH was 6g/L to refine the sponge indium. The amount of pure indium was obtained 17.69g/L with a purity of 3N. In recycling indium from ITO wasted mud, the addition of Zn was 3g/L to replace the sponge indium and the operation temperature was 60°C. Besides the addition of

KOH was 5.33g/L to refine the sponge indium. The amount of pure indium was obtained 5.39g/L with a purity of 99.7%. In this article, the recycling process involved electrochemical technology, vacuum smelting technology, thermodynamic theorems and microstructure analysis. Therefore, we detailed to study and discuss the behavior and characterization of indium by electrochemistry and thermodynamics.



誌謝

兩年的碩士學位得以完成，首先衷心感謝指導教授朝春光博士與劉增豐博士，感謝您在這兩年來對學生耐心的指導與解惑，不管是學業上及未來生活上對學生的關心，在此謹獻上學生由衷的謝忱與敬意。

在學位口試期間，承蒙勝華科技資深處長黃俊銘博士撥空蒞臨指導，對本論文提供多方面的建議與指正讓論文內容能更加完整及嚴謹，在此學生僅致上由衷的謝意。

兩年碩士生涯中首先感謝實驗室建仲學長，在實驗上的幫助並且鼓勵督促我使我遭遇挫折仍能樂觀以對。而在實驗技巧上的提點及英文撰寫的評點方面要感謝士勛學長，總能給予我很大的啟發並且孜孜不倦的修改我的第一篇英文論文，真是辛苦了!謝謝實驗室同伴仕漢、大緯、郁祥，隔壁的張小瑜、呂小錚、柚子寶、ppp 還有陳剛好同學，使我在實驗室這段日子聊天打屁每天都過得很開心。還有應化系的喬盈學妹、剛當上爸爸的陳進興先生，在我去串門子時能熱情的招呼我，很感謝你們!還有實驗室學弟妹佑慈、哲毅、亮延、柏叡，隔壁實驗室的學弟妹境好、馬特，謝謝你們的幫忙與協助使實驗室可以順利進行研究。感謝好友玉芬、游拉風、小牛、譽馨、嘉麗、振瑋、gb 在兩年碩士生活中不斷給予關懷與鼓勵，僅此一併感謝。

兩年的碩士生活匆匆飛逝，在求學生涯中最要感謝的是我的家人，尤其是我的父母親。你們辛苦的養育我、支持我、鼓勵我，使我在求學過程中可以無後顧之憂，也是我最強的後盾，我永遠愛你們!同時也要感謝男友敬懿，有你在身邊讓我學會了包容與體諒，使我能勇敢面對未來的挫折與挑戰，真的謝謝有你如此重要且絕對的存在，感恩你!最後還有我親愛的哥哥，與你一同聊 skype 的日子很開心，感謝你聽我發牢騷和打蟑螂的小事，有你一路支持與陪伴，才能讓我專心且順利的完成學業。

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Chapter 1

Introduction

1.1 Motivation

In recent years, the TCO (transparent conducted oxide) films were widely used in the field of FPD (flat panel displays), because the TCO films have some practical characters like good conductivity and high transparency for visible light. The kind of films was used as a coating layer for display of computers and other electronic device, such as cell phones, instrumentation panels, CD players, etc. [1] There are many forms of TCO, such as AZO(Al-Zn oxide), ATO(Sb-Sn oxide), and FTO(F-Sn oxide), but ITO(indium tin oxide) might catch the most attentions due to its unique properties of transparency and conductivity. In the table 1-1, the comparisons of various TCO films were showed as follow.

Table 1-1 The comparisons of various TCO films [2]

comparison catalogs	AZO	ITO	FTO
Properties	<u>ZnO-base, dope Al</u> 6×E-4 Ωcm (2%Al) 80% (in visble)	<u>In₂O₃-base, dope Sn</u> 3×E-4 Ωcm 85%(depended on substrates, in visble)	<u>SnO₂-base, dope F</u> 90% (in visble), 1.5×E-2 Ωcm used in DSSC (dye sensitized solar cell)
Disadvantages for fabrication	The large dense thins are necessary (by sputtering)	ITO targets was used over 70% , depended on world output	F would make the materials toxic

Among all TCO films, the ITO occupies the most significant application in the field of FPD markets. At 1968, Boort and Groth [3] of the Holland Company discovered the ITO, a kind of low resistance and transparent conducted material, and its resistivity is about $3 \times 10^{-4} \Omega\text{cm}$. In addition, the value is nearly the same with that of metals; the excellent property of conduction make the kind of thin film be used extensively. ITO targets commonly used in FPD markets; furthermore, the world consumption of indium is also over 70% till the end of 2008.[4] Because of the fast development of the FPD markets, the large demands for ITO films were expected. In addition, the high transparency of visible light and ability of infrared reflection widened the more applications for using the ITO films. In recent five years, the main stream still focused on the ITO films and the demand for indium was increasing gradually.

Developments of FPD industries have been investigated for several years. From the fabrication of flat panel display, the better films would be needed relatively. In order to ensure the transparency and conduction of the thin films, most of industries selected the ITO films as the sources materials. The sputtering process to deposit ITO onto glass is inefficient. A large number of rejects are unsuitable for fabricating the display screens. The rejects were usually in grinding sludge or on the shields of the sputtering chamber wall. [1] Besides, the abundance of indium in earth crust is very small and dispersed. Indium is such a rare element and would not be mined in our country; most of indiums are compounded with the metal ores like Zn and Pb. If the inefficient ITO deposition and the increasing demands of indium kept on, the upgrade of industry would be limited seriously. Therefore, recycling indium became a significant issue for the whole environment in this century and the main topic

[4] in the nearly future.

Two methods to recycling indium are introduced, one method is electrolysis and the other is vacuum distillation. [5] In the method of electrolysis, the metal indium could be attained a 99.99% purity and obtained at least 0.5 ppm each of impurities, such as Si, Fe, Ni, and Cu...etc. An abnormal increase of Si content in the final product and the difficulty of preserving high-purity indium for a long time caused the process inefficient. In the method of vacuum distillation, a purer indium could be gotten by the two-step thermal purification. The key problem for the method is only the impurity with lower vapor pressure than indium could be separated away, so those with higher vapor pressure could be separated in other ways to yield indium. Therefore, the method of hydrometallurgy and pyrometallurgy was used to recycle indium from ITO wasted solution in the article. The oxide layer of indium could be eliminated after annealing. The purity of indium could be maintained for a long time and no obvious impurities would be produced during the process.

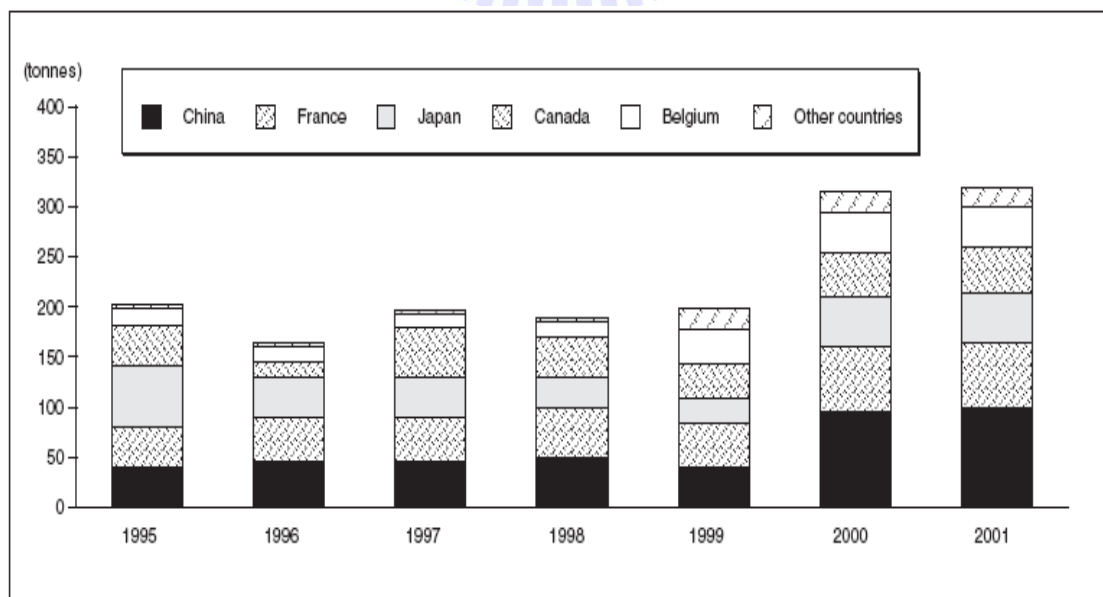


Fig. 1-1 the refinement situation of world countries (1995~2001) [1]

World refinery production was estimated at 200 tons at 1996. In the fig.1-1, the world countries included China, France, Japan and Canada established the processes of refinement in the early 1995. There are eight major producing countries; the top four, Canada, France, Japan, and Russia accounts for 75% of the total. China was the first country to refining indium from the year 1995 because of the abundant quantities and scales of factories. Another important country is Japan, which has the world's largest consumption of indium. [6] The development for ITO is so prosperous that the work of indium refinement would be the next current trends. In addition, Canada has greater resource of indium than any other country-about 27% world storages.

<i>indium (metric tons)</i>		<i>2005</i>	<i>2006</i>	<i>2007</i>	<i>2008</i>	<i>2009</i>
sources {	Virgin	429	497	476	518	551
	Reclaim	357	503	650	802	961
uses {	FPD	595	774	928	1114	1281
	Other	181	188	210	245	274
annual net*		10	38	-12	-39	-43
cumulative**		23	61	49	10	-33

Fig. 1-2 the indium supply and demand forecasts [4]

The figure 1-2 was done by the association of ICA (The Indium Corporation), established in 1934, investigating potential uses of the element indium. The future trends are influenced by many factors:

- (1)World economy in general
- (2)Specific industries trends (e.g. the mining, electronics or energy sectors)

However, additional virgin outputs coming from increased efficiencies and

treatment of residues would cause “the demand market.”

The goal of this research is to establish a process for recycling indium. The problem must be solved by separating In and Sn first because the two elements had some familiar properties and easily compounded with each other. In semiconductor industries, the standard recycling processes were applied to recycle many economical metals, such as W, Mo, Bi, Au, Pd, Pt...etc.[5] The recycling wasted solution could be HCl, H₂SO₄, H₃PO₄, and HNO₃, but the cyanide solution was not suitable to apply these procedures due to its toxic character. The cyanide often used to recycle the rare and precious metals, such as Au, Pd, and Pt. [5] No toxic cyanide in those reclaiming procedures make the experiments safe and practicable.



Chapter 2

Literatures Review

2.1 Background of indium

Indium, which discovered by Ferdinand Reich and Theodore Richter[7], was be identified as a by-product of a wider range of commercial ores including tin (stannite and cassiterite), copper (polymetallic ores), zinc (sphalerite), and lead (galena)...etc.[8] Indium originally would be extracted from zinc and lead ores because of the primarily economic reasons. In addition, indium was found to be a minor component in zinc ores, but market supply was mainly depended on the requirements of zinc market. Furthermore, indium appears widely dispersed on the earth surface, is estimated to be 0.05 ppm for the continental and 0.072 ppm for the oceanic crust, respectively. [4] Because the abundance of indium is so imbalance, the supply around the globe is in terms of geography and political policies.

In the early 1990s, a sudden rush of research for ITO, the potential of thin film technology would be discussed widely. The ITO films consisted of 90% In_2O_3 + 10% SnO_2 . Surge in demand for indium caused the price of In increasing. [4] World production of indium was 173 tons in 1996. (66 tons from the European Union, 40 tons from Canada, 25 tons from China, 20 tons from Japan, 18 tons from the Community of Independent States, and 4 tons from Peru.)[6] The indium was used in making bearing alloys, germanium transistors, rectifiers, thermistors, and photoconductors. Indium could be plated onto metal and evaporated onto glass to form a mirror as good as those made of silver with higher resistance to atmospheric corrosion photocells. In the Fig.2-1, it

presented the consumption situations of indium for some countries. Russia, Canada, and China would be the three large consumption countries in the early 1996.

Table 2-1 The consumption of indium for various countries [6]

Class and country	1995		1996	
	Quantity (kilograms)	Value (thousands)	Quantity (kilograms)	Value (thousands)
Unwrought and waste and scrap:				
Belgium	4,030	\$1,120	2,600	\$748
Cameroon	--	--	112	29
Canada	32,800	12,700	13,000	3,780
China	14,500	6,390	1,700	768
Finland	--	--	21	10
France	4,770	2,020	5,420	2,360
Germany	2,670	537	202	24
Hong Kong	1,450	555	194	80
Israel	--	--	170	36
Japan	3,620	1,370	679	265
Lithuania	75	18	--	--
Netherlands	--	--	276	93
Peru	1,630	705	2,480	757
Russia	14,300	5,420	5,900	2,930
Spain	1,450	465	--	--
Switzerland	2,000	884	--	--
United Kingdom	1,810	809	486	214
Total	85,200	32,900	33,200	12,100

Tin and indium have many familiar properties, such as melting point, boiling point, density, crystal structure, and atomic diameter...etc. The crystal structure of indium is tetragonal. (a: 325.23 pm, b: 325.23 pm, c: 494.61 pm α : 90.000°, β : 90.000°, γ : 90.000°) The Table 2-2 showed the comparison with In and Sn.

Table 2-2 The comparison of the two elements

Item	Density (g/cm ³)	Melting point (°C)	Boiling point (°C)	Oxides	Crystal structure	Atomic diameter (Å)	Reduction Potential (V, SHV)
In	7.31	156.6	2072	InO, In ₂ O ₃	Tetragonal	3.1	-0.139
Sn	7.31	231.92	2062	SnO, SnO ₂	Tetragonal	2.9	-0.136

2.2 Refinement background and applications of indium

Indium is a rare element and ranks 61st in abundance in the Earth's crust at an estimated 240 parts per billion by weight. [9] It is about three times more abundant than silver or mercury. Indium is available in several forms including bar, pieces, powder, nanosize activated powder, rods, shot, sheet and wires; it is a very soft, silvery-white metal with a brilliant luster. In the section 2-1, indium was usually discovered predominantly in zinc-sulfide ore mineral, the sphalerite. The recent applications for indium are as follows (until the end of 2007): [9]

1. ITO targets (70%)
2. Electronic and semiconductor (12%)
3. Solders and low-melting-point alloys (12%)
4. Research (6%)

Let's firstly focus on the third point, the applications for low-melting-alloy system. After developing lead-free solders for electronic application, several

indium-base systems including tin-indium, tin-zinc-indium, tin-silver (-antimony)-indium, and tin-bismuth-indium were presented. These researches achieved the potential applications in communications and transportation in the industrial laboratories. Indium is also used as a strengthening agent for lead solders and as the base material for many low-melting-point solders due to its flexibility (over a greater temperature range) and the character of low-melting-point. [10-13] In addition, while the WHO claimed to stop using lead solders, indium became the maintenance for lead-free solders.

Since the cost of fuel is getting high in the recent ten years, the substitution was found increasingly. Especially, the solar cell researches were turned into a hot issue recently; they are the fundamental source and would not be tired out for a long time.

When the energy on the earth would be exhausted one day, some experts predicted the solar cell industry would increase the requirement of copper-indium-diselenide.[14] The development of solar cell from indium, mostly solar cell was made of silicon wafer in the past. Using the silicon wafer as the substrates of solar cell had some advantages, such as low cost of equipment, high yields from process, fast producing rate, and good translation efficiency. Therefore, Si wafers would be predicted as the main stream for the solar cell market. Recently, many countries in the world tried best in the thin-film solar cell because of the lack of poly-silicon. A thin-film solar cell was made by sputtering multiple layers, which could induce photoelectric effect on the substrate of metal, glass, and plastic...etc, and its thickness is only several micrometers. This new material is much thinner than the original silicon wafer, and the consumption of silicon wafer would be decreased. There are two semiconductor compounds, CIS (copper indium diselenide) and CIGS

(copper indium gallium diselenide), for producing thin-film solar cell. These semiconductor compounds have wide absorption range and good stability. Nevertheless, there are two disadvantages for CIS and CIGS. One is the lifetime; traditional solar cell could use about 20 years, and the life time of thin film solar cell is shorter than 10 years. Because the translation efficiency of thin film solar cell was lower than that of silicon wafer, the large area for thin film solar cell would be required. The other is the cost; costs of thin film solar cell are lower than that of the traditional solar cell, but the equipments for sputtering costs are much higher. Therefore, total cost of fabrication process for thin film solar cell would not be declined. For these reasons, there is still much dilemma for developing the CIS and CIGS thin-film solar cell. The developments for all kinds of thin films solar cell would be depicted as following Fig.2-1. The light-blue line represented the CIGS films. In the future, developing new sources and reducing expenses of indium are other important issues.

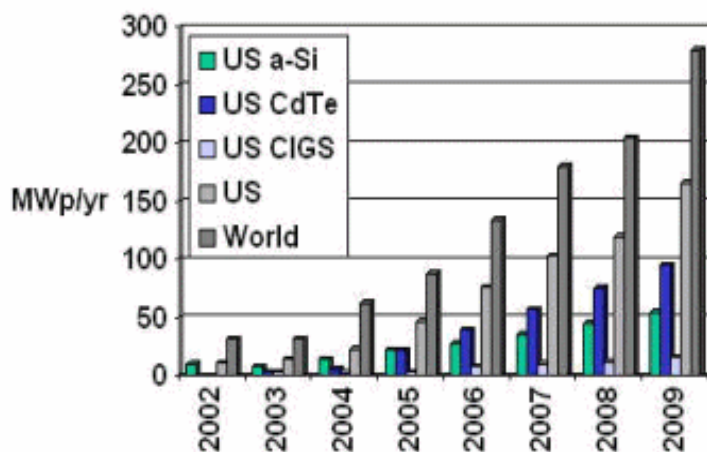


Fig. 2-1 The forecasts for products quantities of thin film solar cell [14]

2.2.1 Refinement background of indium

The American government established an association named the Indium Corporation (ICA) at 1934 to investigate potential uses of the element indium. The association offered over 72 years of indium refining, processing, fabricating, and application engineering experience. [4] As the demand for indium was increasing, more countries were investing lots of efforts to find efficient way for recycling indium. All we want to do is not only extracting them from ores, but also refining out other impurities from primary indium. Base metal smelters were improving the extraction process of indium from ores & minerals, which concentrating with low indium contents. In addition, these smelters are now more aggressively seeking and purchasing indium containing concentrates from various sources. Refining capacity has been increasing on a worldwide. In 2004, Korea Zinc installed a brand new extraction and refining processing line at their zinc smelter. Dowa Mining increased their indium capacity in Japan. Others have installed refining lines to purify crude indium into higher purities. [4]

Recycling became very significant for the first time in 1996 [6] and affected the market and prices. Recycling of indium could expand rapidly if the current price of indium is sustained or continues to increase. The current processes of extracting indium were shown in the figure 2-2. Many countries had an aggressive recycling program that made up for any shortfalls in domestic production and imports of indium. [4]

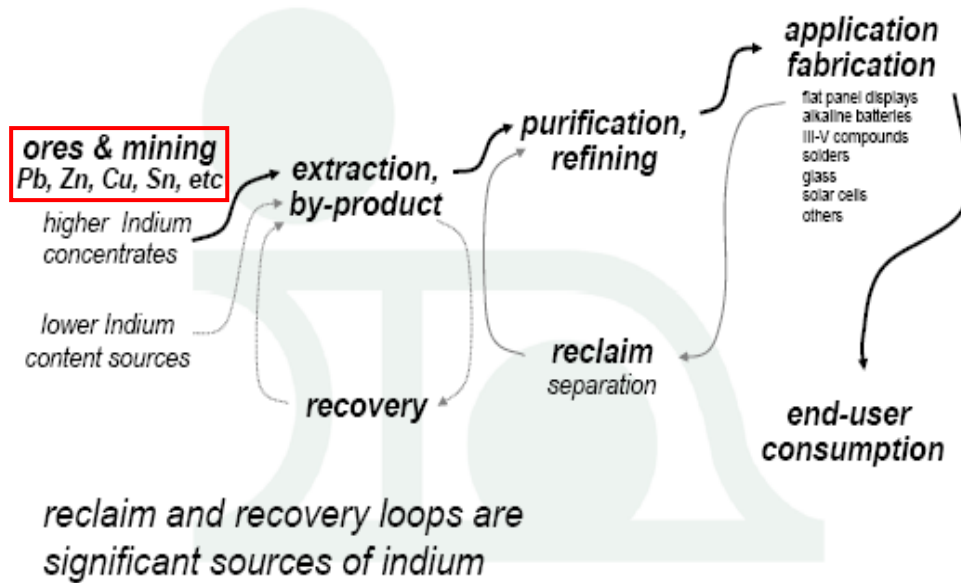


Fig. 2-2 The current extracting process and applications of indium [4]

2.2.2 Methods of refinement high purity indium from ITO wasted materials

In the section, three methods, which could be used to refine indium, would be introduced. The United States Patent No.060580 offered some methods, such as electrolysis, vacuum distillation and zone purification...etc.

2.2.2.1 Electrolysis

In the methods of electrolysis, the metallic indium would be obtained a purity of 99.99 % (4N), and contained at least 0.5 ppm each of impurities such as Si, Fe, Ni, Cu, Ga, and Pb. The purification from waste compound semiconductors had the problem that large equipment and prolonged time was needed to separate and recover indium. Even if the United States Patent showed the production of 4N-purity indium, pure In couldn't maintain for a long period because of an abnormal increase in the Si content of the final. [5]

2.2.2.2 Vacuum distillation method

In the method of vacuum distillation, the pure indium would be attained by two-step thermal process. [5] Indium in an “indium feed” was evaporated and then condensed for recovery in the first thermal purification step. In the second thermal purification step, the product of the first step would be separated from impurity elements of lower vapor pressure and the recovered indium was heated. Basically, In could evaporate away impurity elements of higher vapor pressure at higher temperature. As a result, not only the impurities elements with lower pressure than indium would be found, but also those with higher vapor pressure could be separated in an efficient manner to yield indium with a purity of 99.99% or higher. The central concept of the method was using the different vapor pressures to separate indium from other metals. In addition, some elements with higher vapor pressure than indium are P, S, Cl, P, Ca, Zn, As, Cd, and Pb...etc; and those with lower vapor pressure are Al, Si, Fe, Ni, Cu, and Ga...etc.

2.2.2.3 Zone purification method

In the zone purification method, the purified indium mass had to be cut and there was a potential hazard of contamination [5]; hence, the purification process inevitably suffered from a limited and lower throughput. Furthermore, when the purified indium was cast into an ingot, impurities might enter to cause contamination.

2.2.2.4 Hydrometallurgy and pyrometallurgy method

Among all methods were introduced before, the hydrometallurgy and pyrometallurgy would be the better choices. The hydrometallurgy offered

simple and fast experimental procedures, and the whole process could be finished just for three hours. Comparing other methods of recycling indium, the shortest times also required 15 days. [4] The multiple procedures of other methods made the whole process inefficient and the costs of recycling were getting high. Moreover, the hydrometallurgy with higher chemical selections was suitable to use in the ITO wasted solution. The reducing agents liked Zn and Mg was put in it, and the indium would be replaced gradually. The extra reactions were overlooked by the theorems of electrochemistry except the possible reactions in Zn, Mg, and In. In the research, the hydrometallurgy was first used to recycle the raw indium from the ITO wasted solution. After that, the raw indium was refined by the method of pyrometallurgy, it could avoid other impurities during the process. Therefore, the purity of indium would be attained for a long period. The coherent compositions could be gotten after annealing under the melting point of indium, 156°C . In the chapter three, the detail procedures would be mentioned.

2.3 Thermodynamics theorems and chemical analysis for recycling indium

Many chemical reduction methods were used to extract the indium out from the ITO wasted solution. First, the metals ions with the lower electromotive force could be replaced by the metals with the higher electromotive force from the solution. A few elements which were more activated than indium would be chosen to be the reducing agents. From the pourbaix diagrams, the relative reduction potential of each element could be found, some suitable elements could be selected from the diagrams. Indium would be ionized or oxidized when it was over-potential. In addition, indium

would be deionized to these ions, In^+ , In^{2+} , In^{3+} , and InOH^{2+} when it existed in acidic solutions. Indium would be the oxides, In_2O_3 , when it existed in neutral solutions. Finally, indium would be deionized to InO_2^- as it existed in base solutions. If we want to know the chemical reactions about the atoms, ions, and oxides in aqueous solutions, the electrochemical theorems by the “Nernst’s equations” [15] would be defined as follow:

$$E = E^{\circ} - \frac{RT}{nF} \ln K \quad (2-1)$$

E: reduction potential

E° : standard reduction potential

R: gas constant

T: temperature

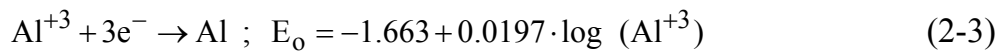
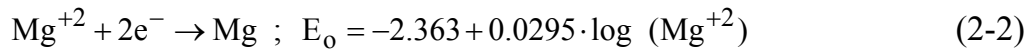
n: the number of interaction electrons

F: Faraday constant

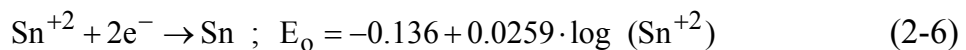
K: the equilibrium constant of ions

The possible electrochemical reactions of indium in the solution were shown in the Table 2-3, and the simpler pourbaix diagram was established according to it. Based on the information of pourbaix diagram of In [16], the metal indium would be the stable In^{3+} ions in acidic solutions. In neutral solution, indium would be covered by an oxide layer on its surface; and the oxide would cut off any reactions between indium and aqueous solution. Indium would be precipitated by the compounds like InCl_3 and InF_3 in the HCl (hydrochloric acid) and HF (hydrofluoric acid), respectively. Both precipitate compounds would not be dissolved in acidic solutions. Through controlling the pH value and electrovoltage of the chemical reactions, indium would be ions in aqueous solutions. Furthermore, the metal indium also could be precipitated on

cathode electrode in the cell by the electrolysis. The specific ions like In^{3+} would be replaced in aqueous solutions at the difference of oxidation voltages of Zn, Al, and Mg, which are -0.76V, -1.67V, and -2.34V. All the voltages are lower than the indium voltage of -0.34V. Therefore, if we put Zn, Mg, and Al plates or powder in aqueous solutions, the indium could reduce ions to metal. The oxidation voltages of above-mentioned:



Another factor to influence the oxidation potential of compound is the concentration of metal ions in solutions. The relationship of oxidation potential and ion concentrations between each element was depicted in the figure 2-3. The magnesium was at the last one and with the greater ability of oxidation than other elements. Tin is the first one and with a lower oxidation potential than indium; therefore, tin was still retained in the ITO wasted solution. As above mentioned, tin and indium have many familiar properties; and a new separation method would be created to extract tin from indium. Eq.2-6 is the oxidation voltage of Sn:



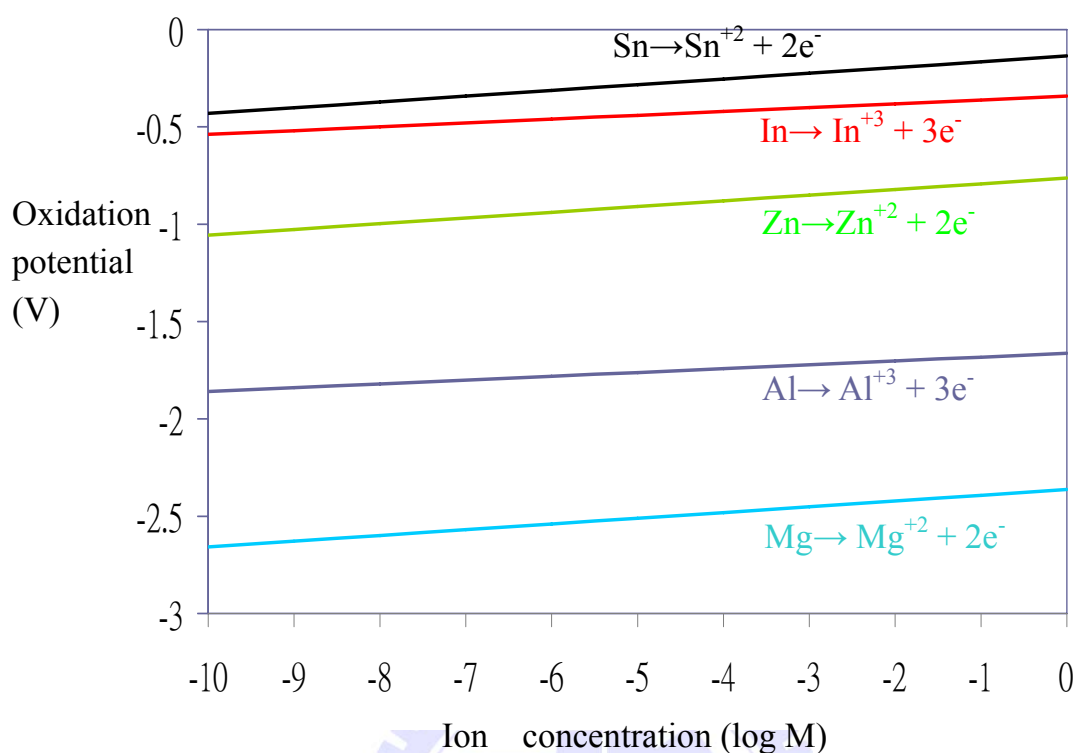


Fig. 2-3 Variation of the oxidation potentials of each element with the relationship of ion concentration

Table 2-3 The possible reactions of indium in the research. [16]

No.	Reaction	Equation
1	$\text{In}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{InOH}^{2+} + \text{H}^+$	$\log \frac{[\text{InOH}^{2+}]}{[\text{In}^{3+}]} = -3.88 + \text{pH}$
2	$\text{InOH}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{InO}_2^- + 3\text{H}^+$	$\log \frac{[\text{InO}_2^-]}{[\text{InOH}^{2+}]} = -20.38 + 3\text{pH}$
3	$\text{In}^+ \rightleftharpoons \text{In}^{2+} + \text{e}^-$	$E = -0.4 + 0.0591 \times \log \frac{[\text{In}^{2+}]}{[\text{In}^+]}$
4	$\text{In}^+ \rightleftharpoons \text{In}^{3+} + 2\text{e}^-$	$E = -0.443 + 0.0295 \times \log \frac{[\text{In}^{3+}]}{[\text{In}^+]}$

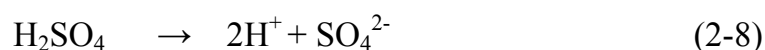
5	$\text{In}^+ + \text{H}_2\text{O} \Leftrightarrow \text{InOH}^{2+} + \text{H}^+ + 2\text{e}^-$	$E = -0.33 - 0.0295\text{pH} + 0.0295 \times \log \frac{[\text{InOH}^{2+}]}{[\text{In}^+]}$
6	$\text{In}^+ + 2\text{H}_2\text{O} \Leftrightarrow \text{InO}_2^- + 4\text{H}^+ + 2\text{e}^-$	$E = 0.262 - 0.118\text{pH} + 0.0295 \times \log \frac{[\text{InO}_2^-]}{[\text{In}^+]}$
7	$\text{In}^{2+} \Leftrightarrow \text{In}^{3+} + \text{e}^-$	$E = -0.489 + 0.0591 \times \log \frac{[\text{In}^{3+}]}{[\text{In}^{2+}]}$
8	$\text{In} + 3\text{H}_2\text{O} \Leftrightarrow \text{In}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^-$	$E = -0.19 - 0.0591\text{pH}$
9	$2\text{In}^{3+} + 3\text{H}_2\text{O} \Leftrightarrow \text{In}_2\text{O}_3 + 6\text{H}^+$	$\log[\text{In}^{3+}] = 7.73 - 3\text{pH}$
10	$2\text{InOH}^{2+} + \text{H}_2\text{O} \Leftrightarrow \text{In}_2\text{O}_3 + 4\text{H}^+$	$\log[\text{InOH}^{2+}] = 3.85 - 2\text{pH}$
11	$\text{In}_2\text{O}_3 + \text{H}_2\text{O} \Leftrightarrow 2\text{InO}_2^- + 2\text{H}^+$	$\log[\text{InO}_2^-] = -17.05 + \text{pH}$
12	$\text{In} \Leftrightarrow \text{In}^+ + \text{e}^-$	$E = -0.139 + 0.0591 \times \log[\text{In}^+]$
13	$\text{In} \Leftrightarrow \text{In}^{3+} + 3\text{e}^-$	$E = -0.342 + 0.0197 \times \log[\text{In}^{3+}]$
14	$\text{In} + \text{H}_2\text{O} \Leftrightarrow \text{InOH}^{2+} + \text{H}^+ + 3\text{e}^-$	$E = -0.266 - 0.0197\text{pH} + 0.0197 \times \log[\text{InOH}^{2+}]$
15	$\text{In} + \text{H}_2\text{O} \Leftrightarrow \text{InO}_2^- + 4\text{H}^+ + 3\text{e}^-$	$E = 0.146 - 0.0788\text{pH} + 0.0197 \times \log[\text{InO}_2^-]$
16	$2\text{In}^+ + 3\text{H}_2\text{O} \Leftrightarrow \text{In}_2\text{O}_3 + 6\text{H}^+ + 4\text{e}^-$	$E = -0.216 - 0.0886\text{pH} - 0.0295 \times \log[\text{In}^+]$
17	$\text{InH} \Leftrightarrow \text{In} + \text{H}^+ + \text{e}^-$	$E = -1.951 - 0.059\text{pH}$

In addition, the principle of electrolysis was introduced to refine indium. There are many methods, such as electrolysis, vacuum distillation, and chemical replacement could be used to recycling indium. The equipment of electrolysis was easier than other methods so it would be chosen for us. The “first” indium by chemical replacement would be defined as the raw metal indium, with a purity of 95%~99%. The indium with a higher purity about 99.9% would be attained after repeated refining, and the kind of indium was so called “fine” indium. Through the electrolysis process, the raw metal indium could turn into fine metal indium with a purity of 99.999% (5N) at least.

Before electrolysis, these impurities metals such as aluminum, tin, and zinc...etc should be removed. The processes of electrolysis were done by twice or three times, and the high purity indium would be obtained gradually. In the procedures, the high-purity indium plate (about 5N) was used as cathode electrode, and the raw metal indium plate from vacuum pyrometallurgy was used as anode electrode. The electrolyte was the $\text{In}_2(\text{SO}_4)_3$ or InCl_3 solution. The electrochemical reaction was shown as following [29]:

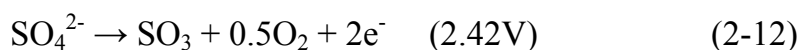
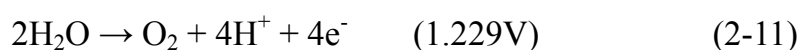
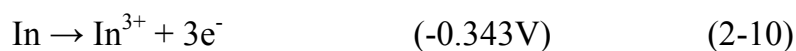


All parts of the electrolyte would deionize in:

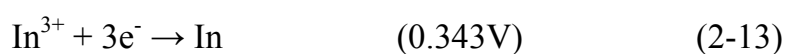


Some electrochemical reactions through external voltages would work possibly.

There are three reactions at the anode electrode were showed as follows:



Some impurities, such as Sn, Bi, Ni, Cu, and Sb, have higher oxidation potential than indium in the anode electrode. Therefore, no compounds would precipitate at the cathode electrode during electrochemical reactions. However, one reaction about aluminum would occur, the oxidation potential of Al was lower than that of In and the compound $\text{Al}(\text{OH})_3$ would be produced in base solution. As a result, the effect of aluminum at the anode electrode could be ignored. The possible reactions were occurred at the cathode electrode:



The standard oxidation potential of hydrogen is lower than indium, and indium would be over-potential and produce In^{3+} by the hydrogen ions. Some hydrogen gas was out in the process of electrolysis. The ion In^{3+} would be reduced and precipitated metal indium on the cathode electrode.

2.3.1 Reagents of indium in the research

The method of replacement was the fast one in recycling indium. A model was used to explain the processes of replacement. Each element with different oxidation potential and the element with lower oxidation potential could be replaced by higher ones. The chemical equilibrium reaction [29] could be expressed like that:

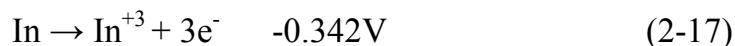


From above reaction, the ion M_1^{n+} was the original ones in the solution, and the element M_2 is the replaced metal added in. The M_2^{n+} was the metal ions replaced from the solution, and the metal M_1 was the element precipitated after replacement. For example, two elements like Zn and In would be used as follow:

The oxidation potential of Zn:



The oxidation potential of In:



The oxidation potential of zinc was lower than that of indium, and indium from ITO wasted solution would be replaced by metal zinc. Then it would be dissolved, the metal indium was precipitated underneath the solution. The chemical equilibrium formula was shown:



Except the element zinc, there were many elements with lower oxidation potential than indium, such as Li, K, Ca, Na, Mg, and Al, whose oxidation potentials are -0.32V, -2.924V, -2.87V, -2.71V, -2.34V, and -1.67V, respectively. [17] These elements all were the reducing agents in the research. There were two reasons of choosing the elements Zn and Mg as the reducing agents. One is the cost; the Zn and Mg powder are cheaper than other elements. The other is the oxidation potentials; Zn and Mg are with lower oxidation potentials than indium. The element like Ca was also with the lower oxidation potentials than indium, but Ca still was unsuitable to as the reducing agent. In the next section, the reason would be introduced.

2.3.2 Pourbaix diagram

The pourbaix diagram could be defined by the thermodynamic theorems in aqueous solution. The ordinate axis of this diagram is the reduction potential E (volts), and the abscissa axis is pH value of solution. A pourbaix diagram was separated into four quadrants: upper left side is acid oxidizing zone, left underneath is acid reducing, upper right side is basic oxidizing, and right underneath is basic reducing. The four quadrants would be used to present the state of some compounds, or the states we wanted also could be observed from the diagram. In the figure 2-4, the pourbaix diagram of Ca [16] would be introduced. The interphase compound (CaH_2) would be produced between the Ca^{2+} and Ca, and it formed at a wide range of pH value. Therefore, it was hard to ignore the appearance of the interphase compound during the reaction $\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$.

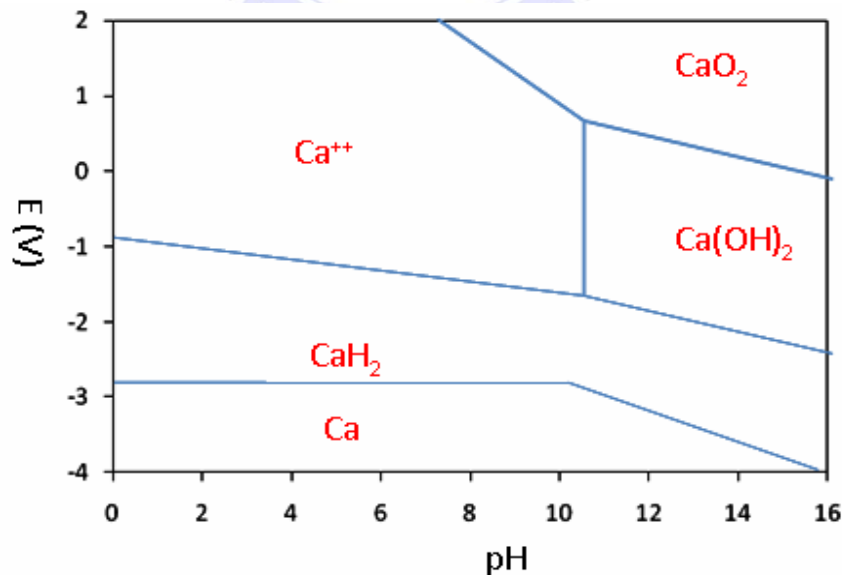


Fig.2-4 The pourbaix diagram of Ca

The pourbaix diagram of In was depicted in the figure 2-5. The In^{3+} would be the ions which existed in the ITO wasted solution. The reaction of $\text{In}^{3+} + 3\text{e}^- \rightarrow \text{In}$ was worked by controlling the fixed electro-voltage. The ion state of In^{3+} should be attained by the state of acid oxidizing; it was the section of upper left side.

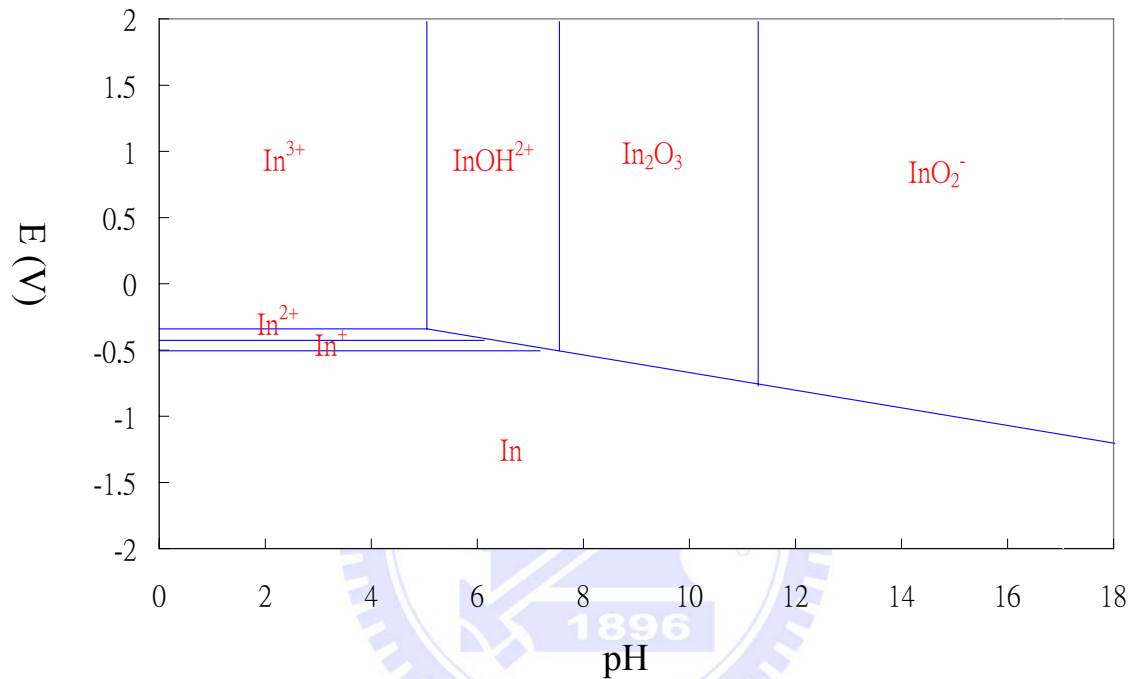


Fig. 2-5 The simple pourbaix diagram for the system indium-water, at 25°C

The only solid compound of trivalent indium which appears in figure 2-5 is the anhydrous oxide In_2O_3 , which is probably the stable form of the oxide of trivalent indium. According to the free enthalpy values, the hydrated oxide $\text{In}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ [or hydroxide $\text{In}(\text{OH})_3$] is less stable than the anhydrous oxide In_2O_3 . [18] Therefore, the stable form of indium oxide is In_2O_3 was depicted in the figure 2-5. In addition, the baths for electro-deposition of indium might be chloride-, sulphate- or sulphamate-based. Indium could also be obtained by reducing its oxide with carbon in a stream of hot hydrogen. Metallic indium is precipitated when excess zinc was added to a solution of an indium salt. [19]

The concentration of In^{2+} was always below the concentration of In^{3+} ions or In^+ ions, and the ion In^+ itself was being the predominant form only at very low dissolved indium concentrations.(below 1.15 mg/l) [20] In reality, In^+ and In^{2+} probably exist as chloride complexes. Remy reported that [21] the oxide In_2O_3 was insoluble in alkali metal hydroxides and ammonia.

2.3.3 The methods of hydrometallurgy and pyrometallurgy in the research

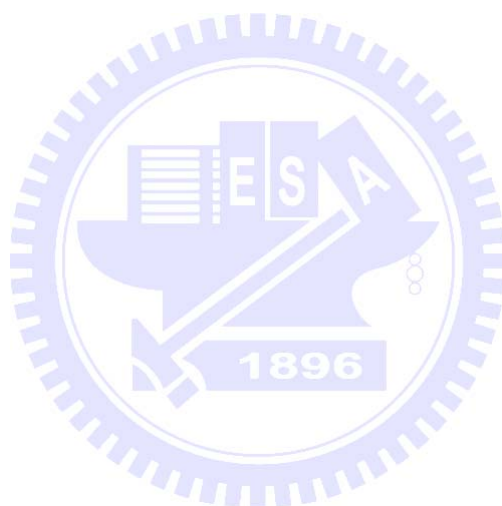
There are some advantages of hydrometallurgy: [22]

- (1) Its economical scales are small, and it has better economic efficiency.
- (2) For the more complex sources of materials, the methods are more suitable in large usages.
- (3) The cost is much cheaper than pyrometallurgy.
- (4) The method could handle the sources with fewer materials.
- (5) This method could operate in atmosphere and room temperature.
- (6) It has the higher chemical selections.
- (7) The method could separate the metals which have similar chemical properties.

Above lists were the reasons to use the hydrometallurgy method. Hydrometallurgy method was used to replace the metal indium from ITO wasted solution, and then the vacuum pyrometallurgy method was used to get the raw metal indium of 2N. Finally, the electrolysis method was used to get the secondary metal indium, high-purity indium of 5N.

Pyrometallurgy was a common method in refining commercial metal for several years. With the slags, the impurities were eliminated at the same time. Evidently, the slags of ITO wasted solution were MgO and NaOH , and the slags of ITO wasted mud were ZnO and KOH . In addition, the metal indium

was surrounded by the oxide, In_2O_3 . The slags were suspended on the top of the melted In and they could be removed by water. Using pyrometallurgy method to refine indium was better because it was convenient and cheap. The whole experiment period just took 2 hours, and the short period provided relative low cost for the research. Hydrometallurgy method with higher chemical selection and pyrometallurgy method with the characters of simple and cheap were the reasons to be used in the research. As a result, the information of electrochemical, thermodynamics, casting, and vacuum pyrometallurgy are used to define these experiment procedures.



Chapter 3

Experimental procedures

3.1 Recycling indium

In this article, the ITO wasted materials included the ITO wasted mud and ITO wasted solution. In order to recycle the pure indium from two kinds of wasted components, the complete experimental procedures were established. The sources of ITO wasted mud were the wasted ITO targets, and those of ITO wasted solution were wasted FPD substrates. After dissolving with saturated HCl, they could be ITO wasted solutions finally.

3.1.1 Recycling from ITO wasted mud

The increasing of the usages in ITO targets caused the appearance of ITO wasted mud. The powder of Al_2O_3 (fine sands) was used to collide the sputtering chamber which deposited ITO films on the glass or aluminum substrates. Therefore, the sands was included many elements in it, such as In, Sn, and Cr...etc. The first step is dissolving the compositions of ITO by acidic solution, the 13 vol% HCl, and it also could be presented to the proportion of HCl: H_2O = 1: 2. Furthermore, the sands could be precipitated underneath the 5000ml beaker, and the process of precipitation took about half or one hours. Then we took the solution out from the beaker and ensured the sands were not retained in it. Keep going on the works of replacing the In^{3+} to metal indium from the solution which be left over. The color change was from dark to light while the sands had few compositions of ITO.

In recycling ITO wasted mud, the slags with KOH were used to extract impurities from pure indium. From the process of pyrometallurgy, we chose the

KOH as the alkali component with slags.

3.1.2 Recycling from ITO wasted solution

In order to establish the complete experimental procedures for extracting indium from ITO wasted materials, the metal indium was dissolved by acidic solution. From the discussion of 3.1, the final forms of ITO wasted materials are the wasted solution after dissolving in the HCl. The wasted materials were dissolved in the 15 vol% HCl (hydrochloric acid) after sieving. In addition, eliminating the ions of indium (In^{3+}) gradually and the color of solution would turn to the light yellow. While getting the solutions, the first thing is testing the compositions of the solutions. If the composition of indium could be known in each solution, the efficiency of recycling would be calculated. Then the color of ITO acidic solution would be showed in the figure 3-1.

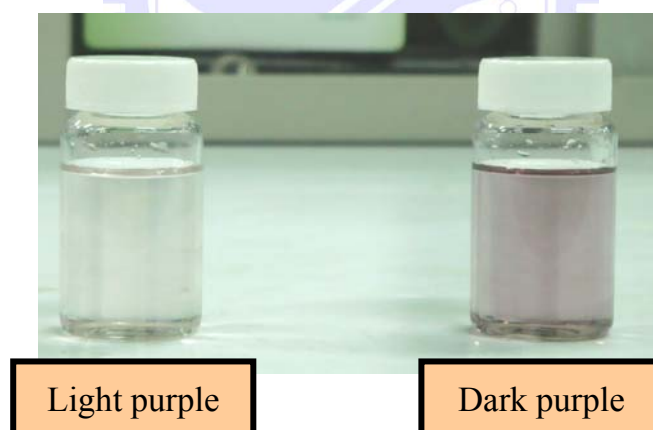


Fig. 3-1 color change of ITO wasted solution

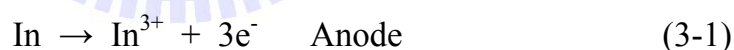
In the fig. 3-1, the left bottle has little ions of indium, and the color is light purple. The right bottle is the original color of solution, and many kinds of ions are involved in it. After the ICP test, the step of chemical reducing would be carried on.

The source of ITO wasted solution was the residues from the substrates of

flat panel displays (FPD). The kinds of ITO wasted materials are commonly existences because of the large amounts of FPD factories. The fragments in the wasted FPD materials have many sizes if they wouldn't be sieved before using. Then we dissolved with 15vol% HCl and the components without the compositions of indium would be precipitated under the solution. Moreover, the slags with NaOH were used to extract impurities from pure indium. After pyrometallurgy, the alkali component like KOH was not suitable to use because the contents of indium were less than the slags with NaOH.

3.1.3 Removal of residual Sn

The element Sn would be gotten rid of before reducing because of the similar properties to indium. The oxidation potential of tin is higher than that of indium, so the element Sn was obtained by oxidizing the In to In^{3+} in the acidic solution. Then Sn^{2+} in the acidic solution was reduced onto the pure indium plate. Although the pure indium plate was slightly dissolved into the acidic solution, the semi- reactions would be introduced as follow.



Then the equilibrium reaction in the system was:



The dynamic balance existed in the system of removal of Sn. The operation condition is at the temperature of 60°C and the time of indium plate was soaked in is about 30 minutes. The figure 3-2 and 3-3 was depicted the Sn powder after reducing and the pure indium plate for substitution.



Fig.3-2 the drying Sn powder



Fig.3-3 the pure indium plate for substitution

In the fig.3-2, the Sn powder with a luster of bright white after replacing. Furthermore, the pure indium plate in the fig.3-3 was produced from the repeating replacing and pyrometallurgy, and it with a purity of 99%. The surface areas should be as large as possible because the soaking areas reflected the reactive regions. The bulk indium was rolled before we used it. The procedure to getting rid of the element tin would be repeated several times, it took about six times for the whole process.

3.2 Analysis

3.2.1 Composition testing by EDX & ICP

The ICP was used to test ITO wasted solution before chemical replacement. The previous concentration of ITO wasted solution was compared with that after reducing. The increase of ions was not only the phenomenon was observed, but the decrease of other element was also an important issue. The units of ICP were the ppm, and the instrument was used to test the liquid solutions.

The EDX was used to determine the accuracy of some materials, was attached to the FESEM system; the model for the instrument is JSM-6500F. The figure 3-4 shows the entire instrument. The purity of indium could be defined by EDX. The selection areas could be a wide range for each sample because the partial higher concentration of some impurities would lead to the deviation for the coherent composition of indium. From the EDX analysis, the image for the sample, the suspension, the sponge indium, the pure indium, and the impurities all could be obtained. The previous preparations for the EDX testing were dried and cut the bulk indium into a suitable mass because the samples of SEM were a ten-dollar size.



Fig. 3-4 The instrument of FE-SEM (JSM-6500F)

3.2.2 Microstructures testing by SEM & OM

The purpose for electro-polishing was used to decrease the damages caused by the mechanical polishing. The mechanical polishing was suitable for the metals which have suitable hardness. Because the metal indium was much softer, the mechanical polishing was not used in the situation. After the electro-polishing of the indium surface, the clear grain boundaries and the shapes of grains were observed. In general, the metal which would be polished was put at the anode electrode in the cell. Then the electric current was passed over, the anodic metal would be dissolved in the cell. The principle of electro-polishing would be introduced in figure 3-5 and 3-6, as follow.

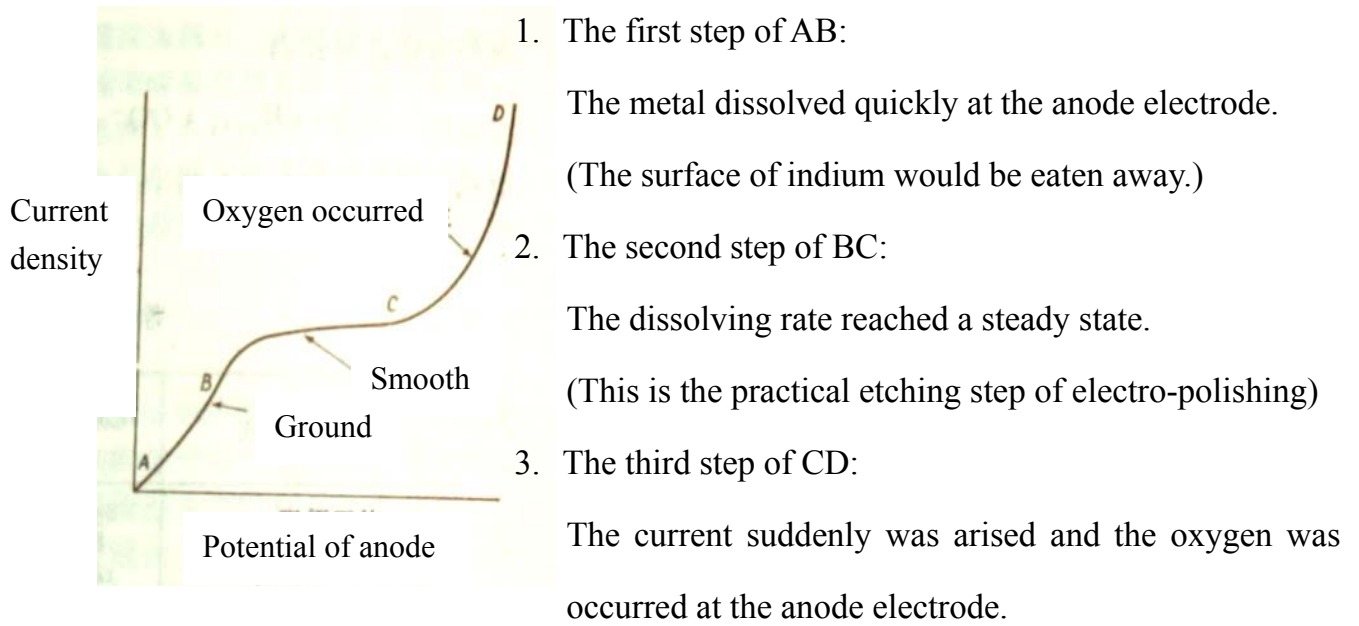


Fig. 3-5 the reaction steps of electro-polishing. [23]

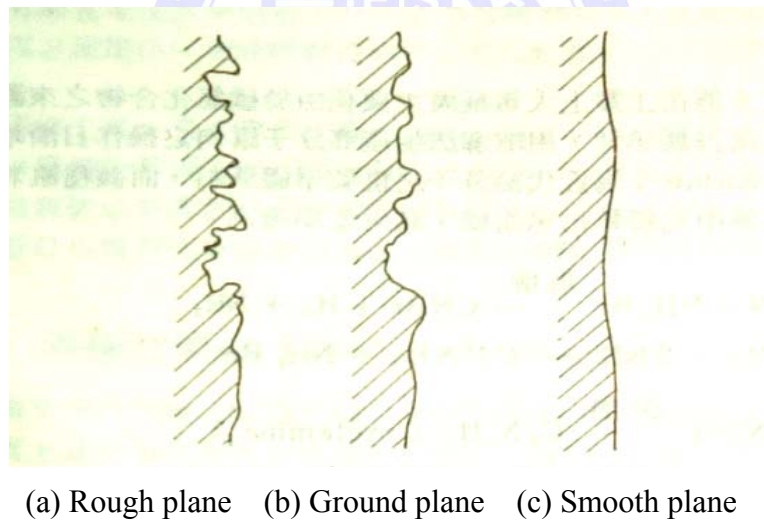


Fig. 3-6 the relative steps of above. [23]

The figure 3-6 is the final state was expected. The slight changes for the indium surface were obtained by the electrochemical method.

The samples of electro-polishing were the same as that of fabricating AAO (anodic aluminum oxide). The fabricating instruments in our labs were already used for several years. Avoid the water and gas, the sample offered an available capacity for the metal indium. In the figure 3-7(a), the indium would be put in the left white holder. The pictures of samples were shown in figure 3-7 (a)-(b).



Fig.3-7 The samples of electro-polishing. (a) The front view of holder and it had a conductive piece of Cu. (b) The holder were used to put the indium in it.

After electro-polishing, the OM (optical microscope) was used to characterize the indium microstructure. The images about grains, grain boundaries, and twins also could be found. These images offered the references for the definition of indium, and the most important definition was the information of EDX. The EDX could provide the statistics of composition, as well as the quantification data also confirmed the result of purity. Finally, the summary of the experiment would be depicted at the figure 3-8.

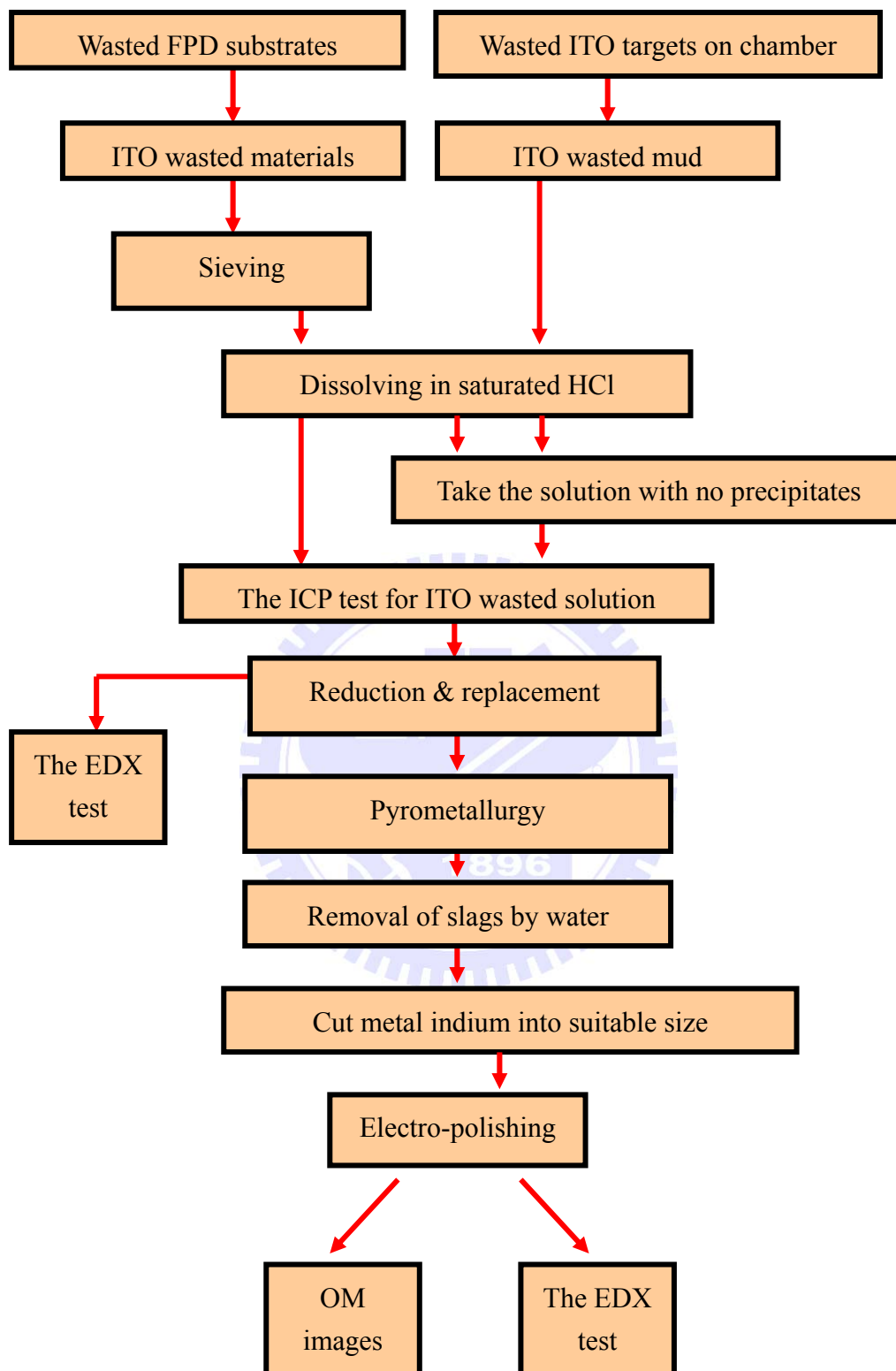


Fig. 3-8 The whole experimental flow chart in the research

Chapter 4

Results and Discussions

4.1 The thermodynamic theorems in the hydrometallurgy

4.1.1 The pourbaix diagram of Zn and Mg

The pourbaix diagram of Zn and Mg was introduced in the section. They are also two reducing agents in the hydrometallurgy, and it pointed out the proper states of Zn^{2+} and Mg^{2+} to replace the In^{3+} from ITO wasted solution. In section 2.3.2, pourbaix diagram consisted of the reduction potential and the pH value was mentioned. If the proper acidic states could be controlled, the In^{3+} ions could be replaced from the wasted solution after adding a suitable electro-voltage. First, the simple pourbaix diagram of Mg was shown in the figure 4-1.

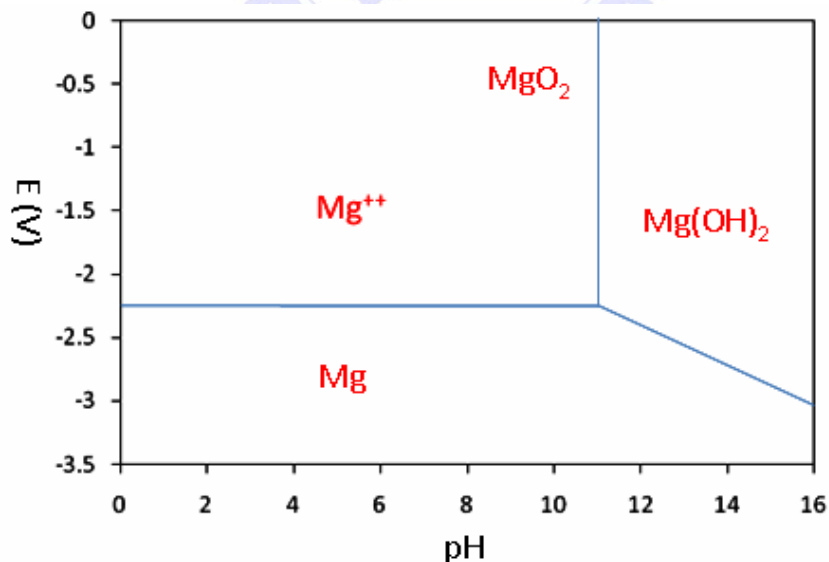


Fig.4-1 The pourbaix diagram of magnetism [16]

Magnesium is a very base metal and also a powerful reducing agent. From the figure 4-1, at pH's above about 8.5 and up to 11.5 it can cover itself with more or less protective oxide or hydroxide which checks the dissolution reaction. On account of the low value of the equilibrium potential of the reaction, it is impossible to prepare metallic magnesium by the electrolysis of its aqueous solution. It would lead to the evolution of hydrogen at the cathode without the formation of magnesium.

In the figure 4-1, it pointed out the oxidation of magnesium in alkaline solution could give rise to the formation of the oxide MgO and the hydroxide Mg(OH)₂, neither of which possesses any amphoteric character. A reaction $MgO + H_2O = Mg(OH)_2$ could present the relationship between the two kinds of compound[24]. In the research, Mg powder was used to recycling the ITO wasted solution.

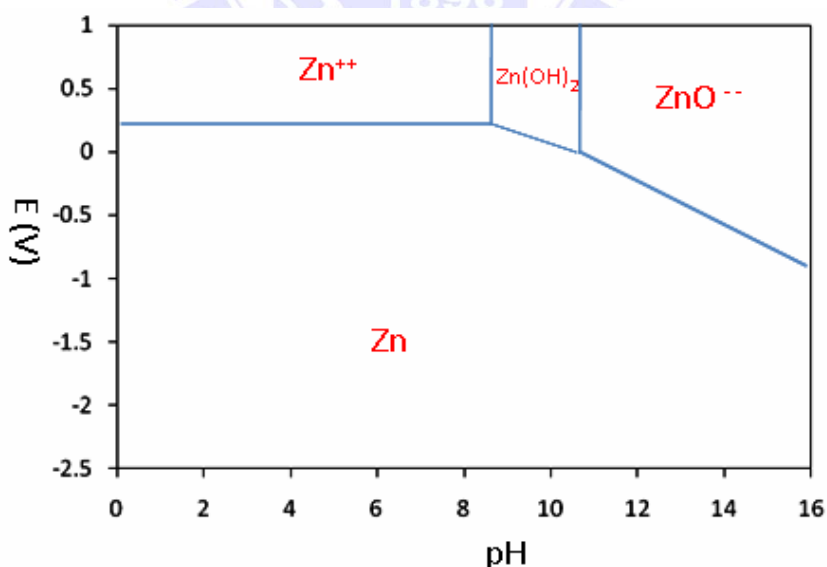


Fig.4-2 The pourbaix diagram of zinc [16]

Zinc appears to be a base metal. In the figure 4-2, the ϵ -Zn(OH)₂ is the most stable form in aqueous solution. In agreement with the value of free enthalpy of formation, -133626 cal, ϵ -Zn(OH)₂ was with the smallest value compared to others.[16] The compound ϵ -Zn(OH)₂ was stable in the alkaline solutions of pH value between about 8.5 and 10.5, and it also should be operated at a suitable electro-voltage. If the zinc is put in contact with a metal of low hydrogen over potential like platinum, an abundant evolution of hydrogen on the platinum then occurs simultaneously with the corrosion of the zinc. [25]

It was possible to produce metallic zinc by the reduction of aqueous solutions of zinc salts. As we knew, this reduction is brought about industrially by the electrolysis of acidic solutions (buffered with acetic acid and acetates) or alkaline solutions (zincates or cyanide complexes). On account of its electronegative character and its small “self-corrosion” [26], zinc was a metal which lends itself well to use as a sacrificial anode for the protection of iron and other metals.

From the fig. 4-1 and 4-2, it was obvious that no interphase compound was produced between Mg and Mg²⁺ and Zn and Zn²⁺. During the process of hydrometallurgy, it's unnecessary to consider other oxidation reactions except those of $\text{Mg} \rightarrow \text{Mg} + 2\text{e}^-$ and $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$. No complex compounds was produced in the replacement, and it is the reason that we didn't choose the element Ca as reducing agent.(in previous section 2.3.2) The table 4-1 shows the comparison of two reducing agents in the hydrometallurgy.

Table 4-1 The summary of two kinds of reducing agents in the hydrometallurgy

catalog of ITO conditions	ITO wasted solution	ITO wasted mud
Reducing agent	Mg, $\psi=325$ mesh	Zn, $\psi=325$ mesh
Heat	No	Yes
ΔH	$\Delta H \ll 0$, exothermic	$\Delta H < 0$, it could work over $T = 60^\circ\text{C}$, exothermic
Shapes of indium After replacement	Sponge indium would be got, the dry powder is soft.	Sponge indium would be got, the dry powder is tough.
Get rid of reagents after pyrometallurgy	It has great oxidation ability, and would be eliminated easily by forming MgO	It has general oxidation ability and would be eliminated by forming ZnO
Organizations from OM	Clear grainboundries	Clear grainboundries & pitting point would be occurred
Slags	NaOH+ impurities	KOH+ impurities
Purity of indium	99.9 wt%	99.7 wt%

4.2 The ICP and EDX results of ITO wasted solution after hydrometallurgy

4.2.1 The EDX results of FPD wasted substrates

The SEM images of FPD wasted substrates were depicted in the figure 4-3 (a)-(f).

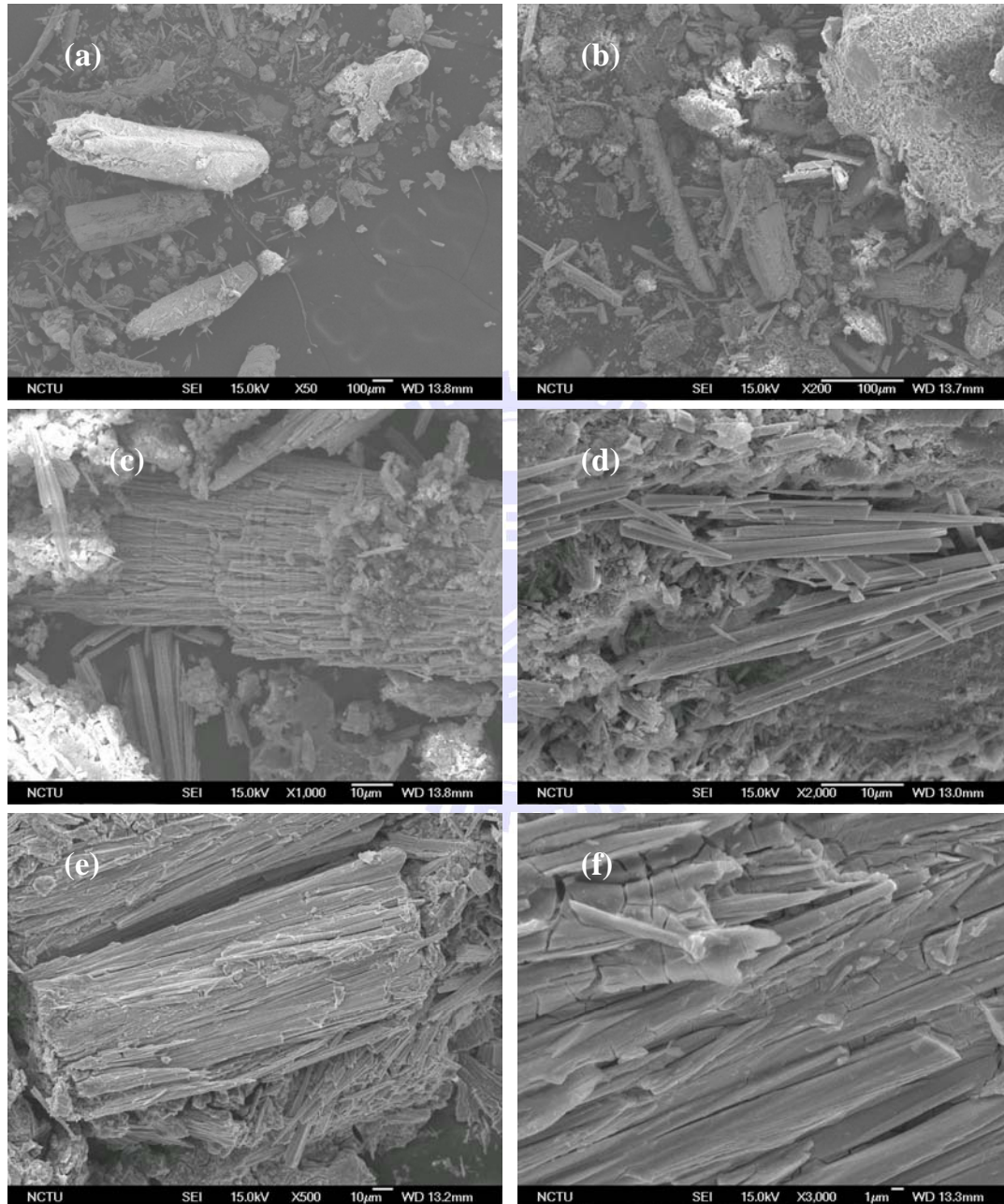
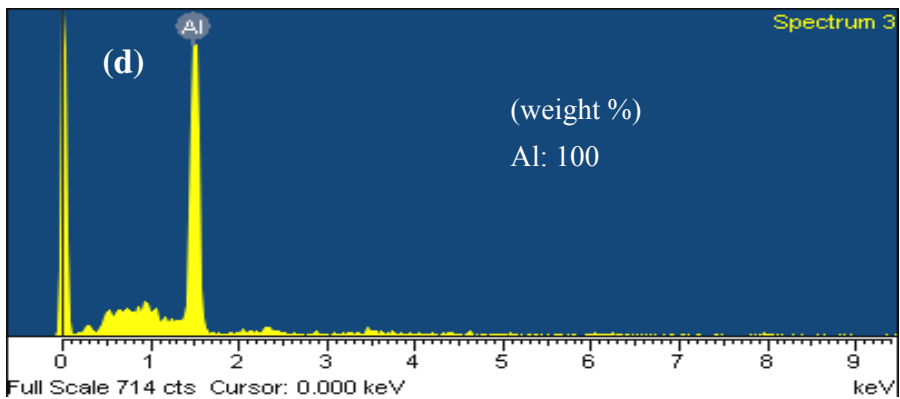
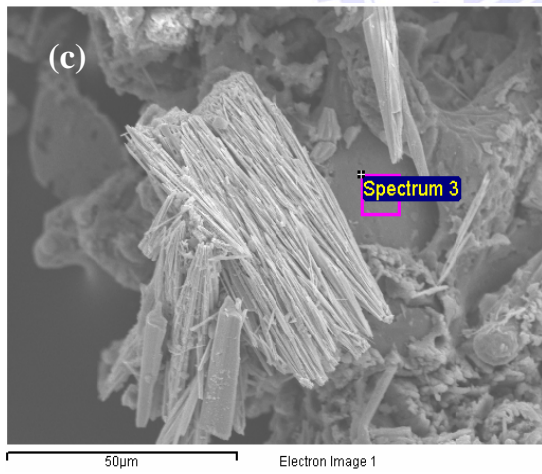
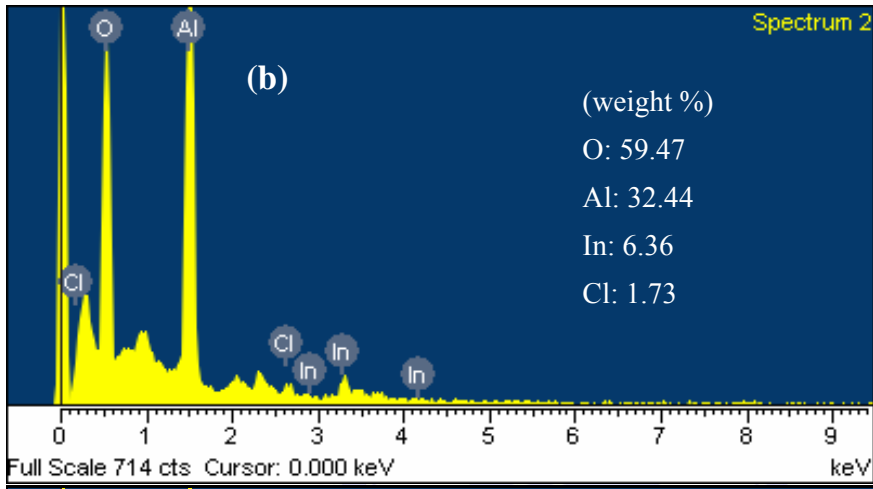
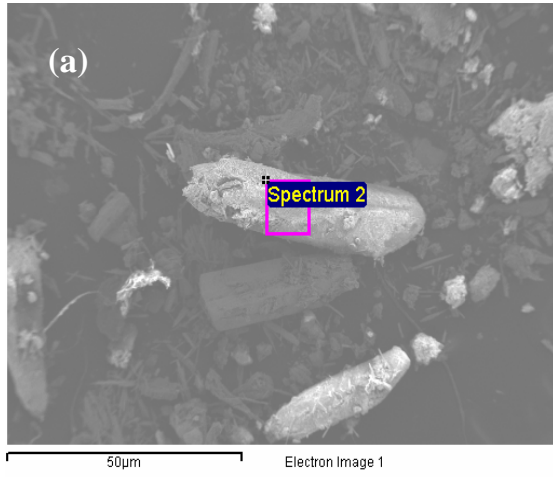


Fig.4-3 The different parts of FPD wasted substrates. (a) Al substrates, 50X. (b) Al substrates, 200X. (c) The ITO films, 1000X. (d) The ITO films, 2000X. (e) The ITO films, 500X. (f) The ITO films, 3000X.



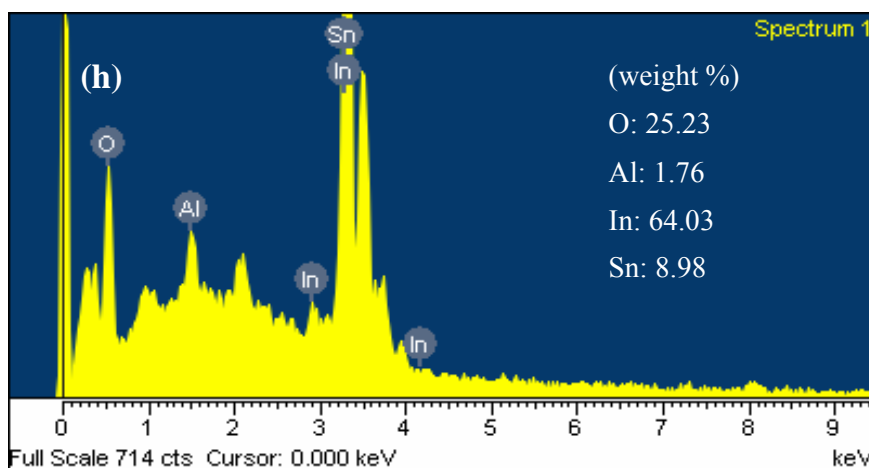
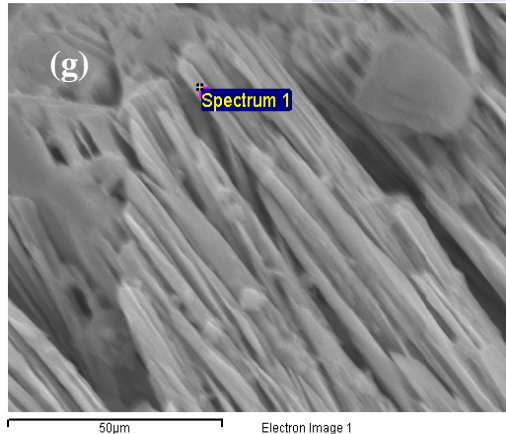
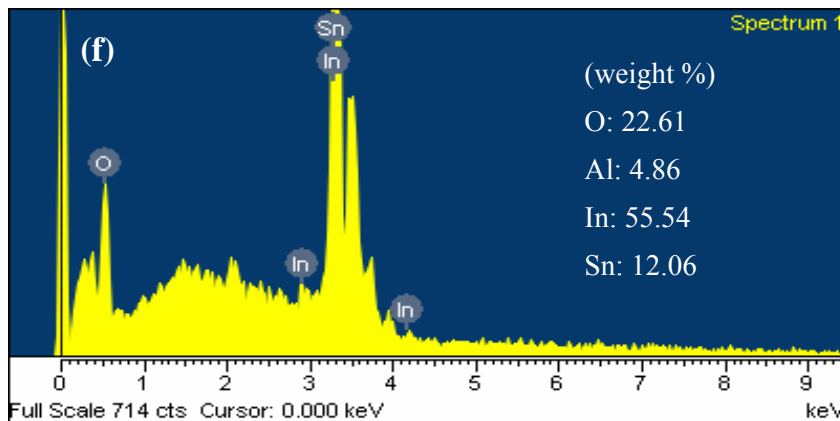
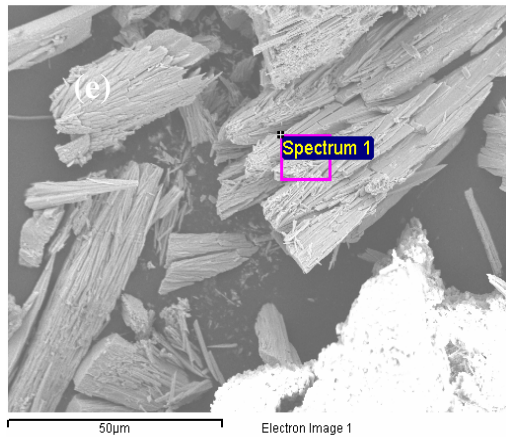
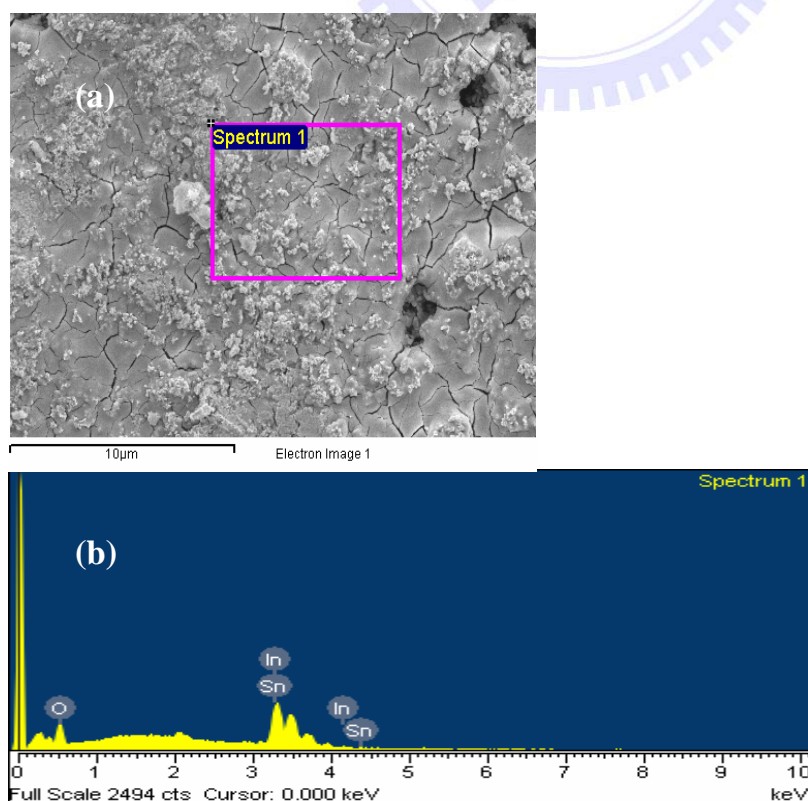


Fig. 4-4 (a)-(h) EDX results of the ITO wasted materials. (a) SEM images of Al fragments. (drug-formed) (b) EDX results of Al fragments. (c) SEM images of Al substrates. (d) EDX results of Al substrates. (e) SEM images of ITO films. (f) EDX results of ITO films. (g) SEM images of ITO films (needle-formed). (h) EDX results of ITO films.

Before making the ITO acidic solution, Al substrates could be separated from the ITO films. According to the figure 4-4 (a), the drug-formed and some large flat regions could be the Al substrates. These Al substrates could be sieved before dissolving the ITO wasted materials. Furthermore, the needle-formed structures could be the ITO films in the figure 4-4 (e) & (g); the proportion for In to Sn is near the composition of the ITO film, consisted of 90% In_2O_3 + 10% SnO_2 .

4.2.2 The results of removal of Sn

The chemical reduction method was used to remove element Sn in the research. The pure indium plate with a purity of 5N could be put in the ITO wasted solution before hydrometallurgy. According to the figure 2-3, the oxidation potential of In is lower than that of Sn. while we operated at the temperature 60°C , the Sn powder would be replaced onto the pure indium plate. The EDX results were shown in the figure 4-5 (a)-(f).



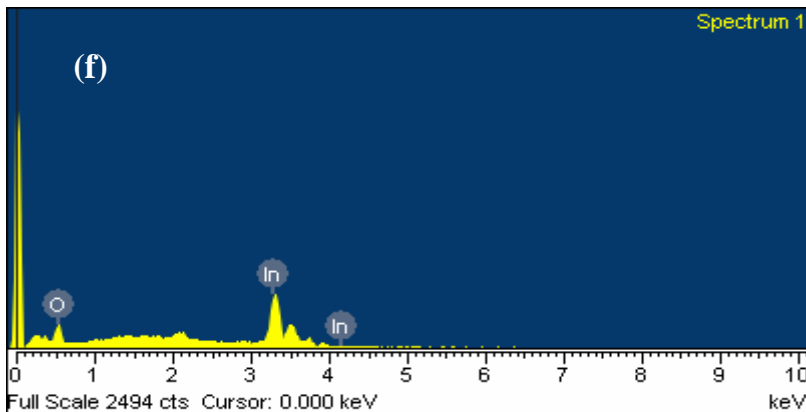
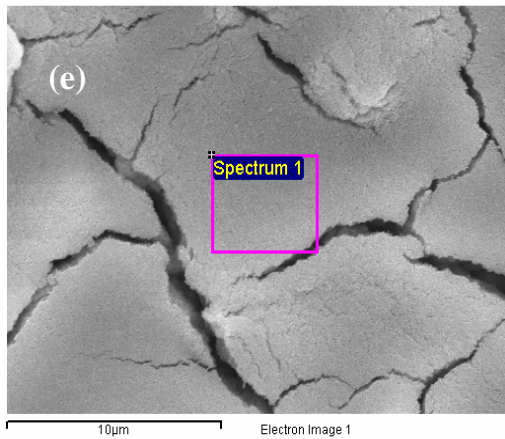
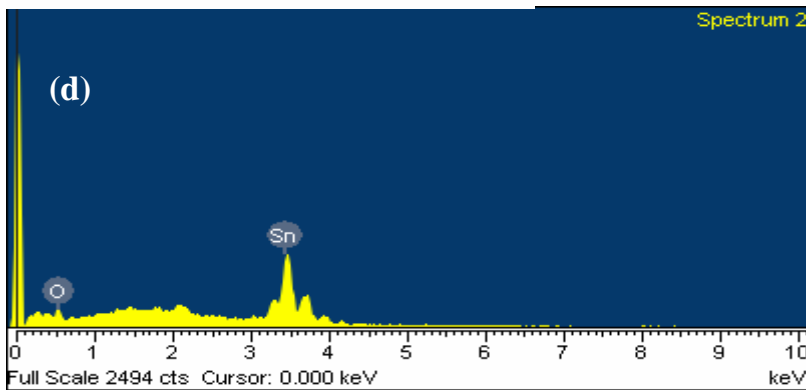
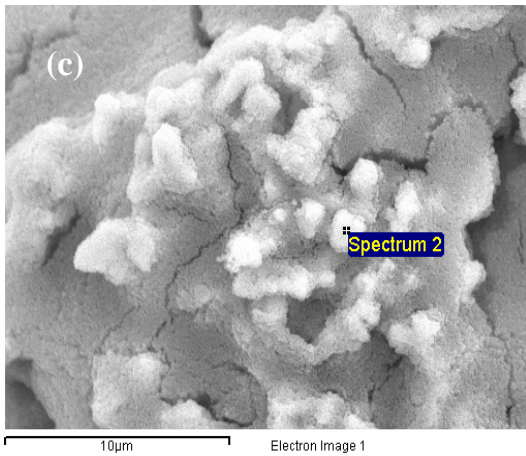


Fig. 4-5 (a)-(f) the EDX results for removal of Sn powder. (a) SEM images of indium plate with Sn powder. (b) EDX results of indium plate, and Sn powder was retained on it. (c) SEM images of the powder onto indium plate. (d) EDX result of the powder, and it was composed of Sn. (e) SEM images of “clean” indium plate. (f) EDX results of indium plate, and it was all composed of In.

In the figure 4-5 (d), the EDX results of Sn were found. Therefore, the composition of Sn was removed completely if the step was repeated several times. No matter in the ITO wasted solution or in the ITO wasted mud, the procedure of removal of Sn was still the step before hydrometallurgy. The results confirmed the pure indium plate was successful to replace Sn from ITO wasted solution.

4.2.3 The ICP results and the analysis of suspension before hydrometallurgy

Table 4-2 The results of ICP test.

Ions	concentration		Comparison results
	before reduction	after reduction	
Al	2.7 wt%	2.7 wt%	The same
Sn	0.8 wt%	0.0 wt%	Decrease
In	4.47 wt%	5.62 wt%	Increase

In Table 4-2, it was used to compare the changes of indium ions after hydrometallurgy. The quantity of indium is obviously large after the replacement from ITO wasted solution. In addition, the quantity of tin ions was decreasing after that. Some components were suspended on the top of solution if dissolving the ITO wasted materials with HCl. The kind of components we called the “suspension”, it consisted of these elements, such as aluminum and tin. It’s useful to decrease the tin concentration in original wasted solution.

The suspension was another way to decrease the quantities of Al and Sn in

the original ITO solution. From the results of EDX, The signals of Sn are larger than that of Al because the quantities of Sn are relatively high. In the figure 4-6 (a) and (b), the suspension of ITO wasted solution was shown. The signals of Al and Sn could be found, and still a signal of Cl⁻ in it. After dissolving in the HCl, some quantities of Al and Sn would be replaced without hydrometallurgy.

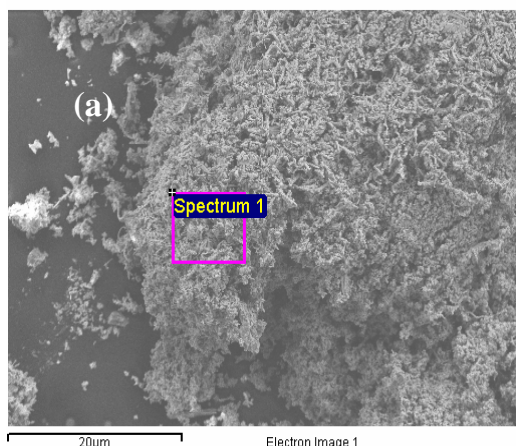
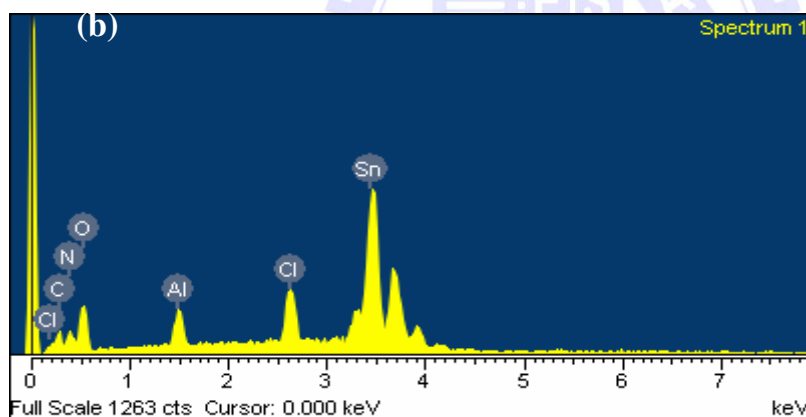


Fig.4-6 The EDX results of suspension. (a) SEM images of suspension. (b) EDX results of suspension, and the signals of Al and Sn were evident.



4.2.4 The EDX results of sponge indium after hydrometallurgy

In the figure 4-7, the EDX results were introduced that sponge indium was replaced by Zn powder. Many kinds of elements, such as Al, Zn, Cl, and In involved in the sponge indium. The purpose of hydrometallurgy was replaced “raw indium” from the ITO wasted solution. In the process of replacement, we stirred the solution and put the reducing agents at the same time. As we stirred the solution, the swirls would make the raw indium congregate. The raw metal indium would be put in the acetone after getting it out of water.

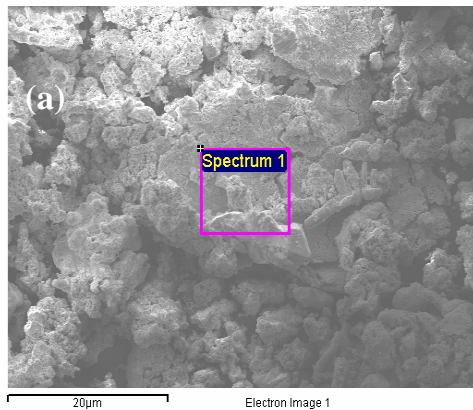
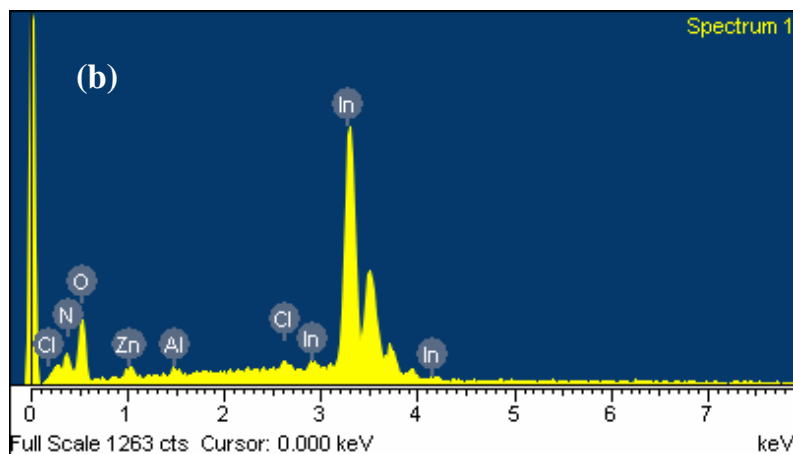


Fig.4-7 (a)-(b) The EDX results of sponge indium was replaced by Zn. (a) SEM images of sponge indium. (b) EDX results of sponge indium, and the raw indium included many kinds of elements.



In the figure 4-8 (a)-(b), the EDX results were introduced the sponge indium which was replaced by Mg powder. The composition of Mg was still retained in it, and the weight percent was about 2.88%. Many elements could be found in the sponge indium, such as Al, Cl, and In. After pyrometallurgy, the pure indium could be attained, and the results were showed in the section 4.4.

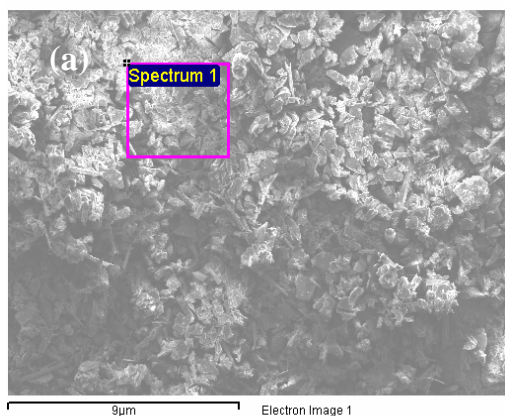
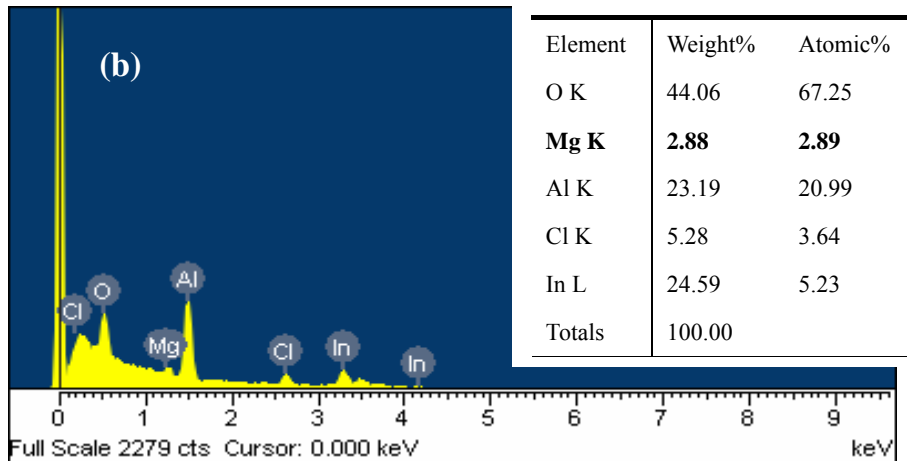


Fig.4-8 (a)-(b) the EDX results of sponge indium was replaced by Mg. (a) SEM images of sponge indium. (b) Residual Mg could be found in the raw indium.



From the figure 4-8 and 4-9, some phenomena could be found. While the indium was still the sponge indium, some elements like Mg, Zn, Al, and Cl were all presented in the sponge indium without doing the pyrometallurgy. Therefore, pyrometallurgy was used to refine the sponge indium, and the impurities were eliminated during the process. During the process, the slags were produced to extract the impurities and the purity of indium was raised.

4.3 The ICP and EDX results of ITO wasted mud after hydrometallurgy

4.3.1 The EDX results of ITO wasted mud

The concept for using sands to collide the inner sputter chamber wall (the residual ITO targets fragments) was for the reason that the inefficient way to use the ITO targets. Then the sands with ITO would be dissolved in acidic solution and make the sands without ITO precipitated underneath the 5000ml beaker. The color change of sands was observed during the process. As the sands without the compositions of ITO, it changed the color of bright white. As the sands with the compositions of ITO, it was the color of dark green. In other words, the color change is from dark to light while the sands had few compositions of ITO.

In the figure 4-9 (a)-(e), the process of recycling indium was introduced as follow.

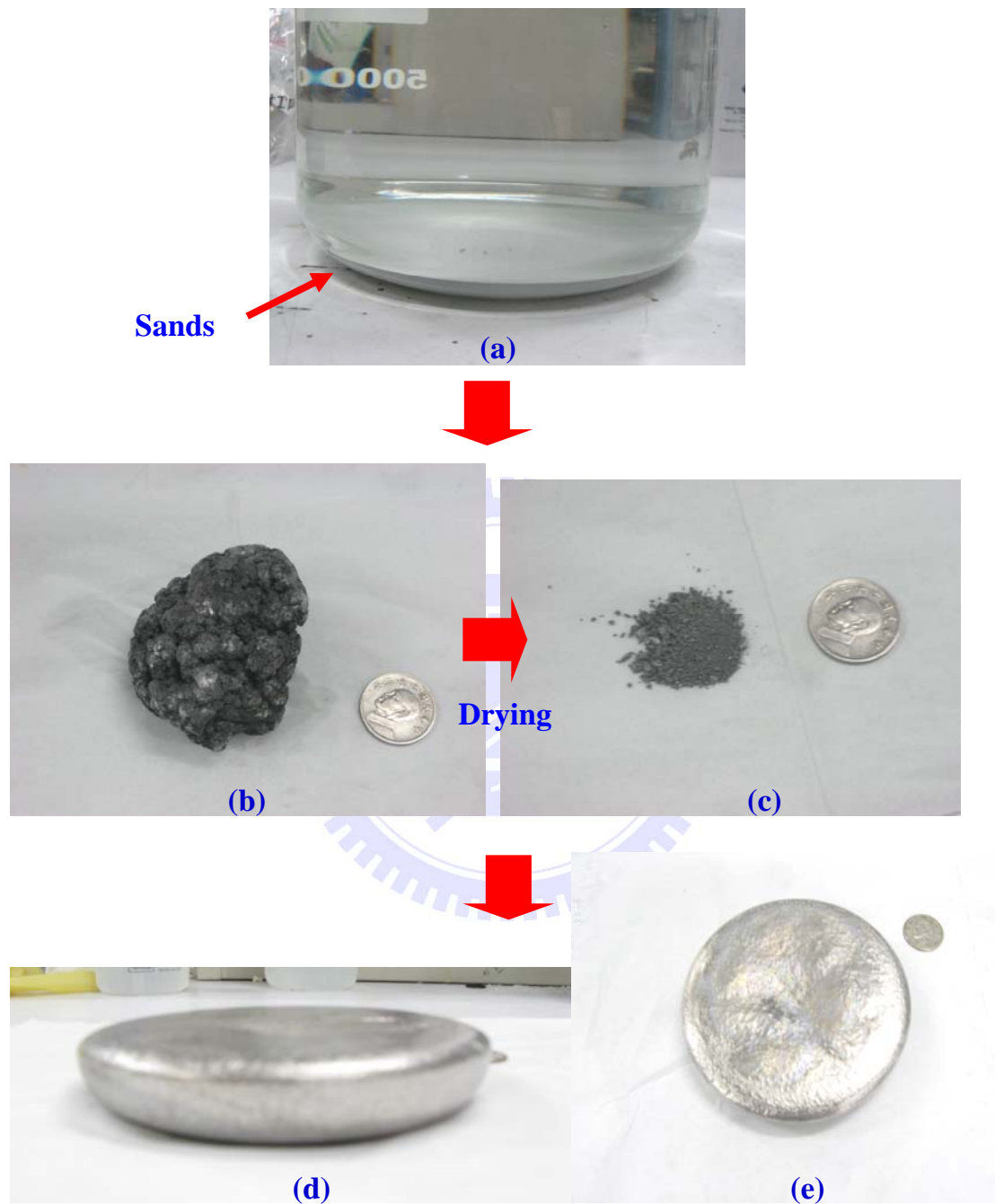


Fig. 4-9 (a)-(e) Pictures of process of recycling indium. (a). The sands would be precipitated underneath the beaker. (b) The sponge indium without drying. (c) The drying indium powder. (d)The side images of pure indium. (e) The front images of pure indium.

The EDX results of ITO wasted mud before hydrometallurgy were presented. In the figure 4-10(a)-(b), the element Cr was found in the sample of mud. The reason for existence of Cr ions is the sputter chambers used to deposit the ITO films was made of the stainless steels. In contrary to the ITO wasted solution, the ions categories are less than that of ITO wasted mud.

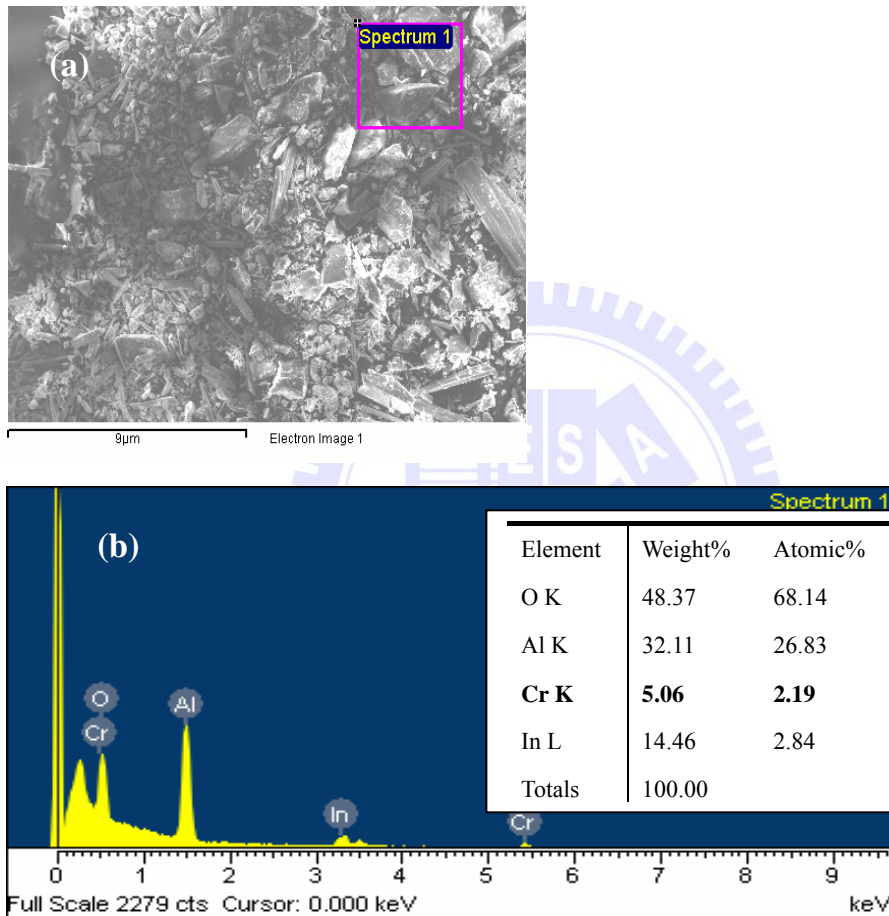


Fig. 4-10 (a)-(b) EDX results of ITO wasted mud. (a) SEM image of ITO wasted mud. (b) Cr ions would be found in it because of the stain steel of the sputtering chamber wall.

4.3.2 The EDX results of sponge indium after hydrometallurgy

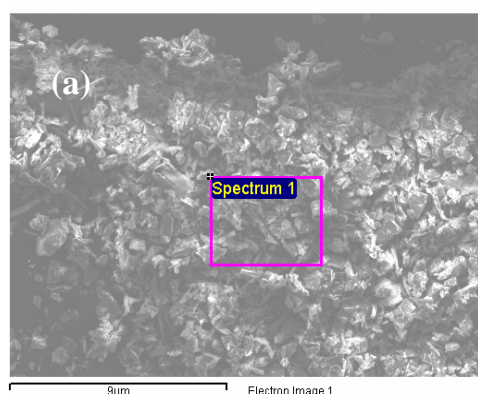
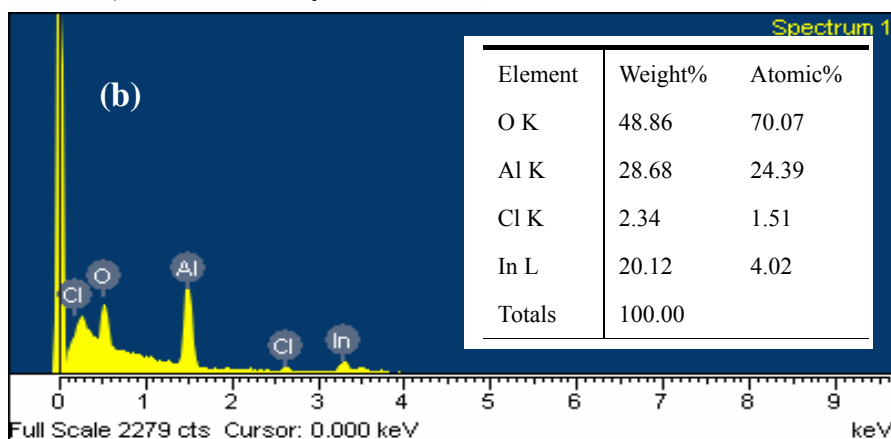


Fig. 4-11 (a)-(b) EDX results of sponge indium by Zn. (a) SEM image of sponge indium. (b) Cr and Cl⁻ ions would be found in the raw indium.

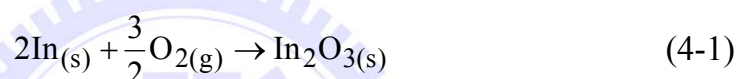


In the figure 4-11, the sponge indium was replaced by Zn powder. According to the table 4-1, the Zn was better reducing agent in the ITO wasted mud. Some element liked Cr would be eliminated after hydrometallurgy, and the elements, such as Al, and Cl were still retained in the sponge indium. The EDX results were presented the Cr element was decreased efficiently after hydrometallurgy. According to the section 2.3, the oxidation potential of Zn was about -0.763V. Because the oxidation potential of Cr was higher than that of Zn, the reaction of $\text{Cr} + 2e^- \rightarrow \text{Cr} (-0.7\text{V})$ was occurred during the process of replacement by Zn. In contrary to the section 4.2.4, the sponge indium from ITO wasted solution included more elements in it. The sponge indium from ITO wasted mud included the basic elements, such as Cl, and Al, and the reducing agents like Zn was not retained.

4.4 The thermodynamic theorems in the pyrometallurgy

4.4.1 The calculations for the possible thermodynamic reactions in pyrometallurgy

While the sponge indium was replaced from the ITO wasted solution, then the sponge indium will be put onto the hot plate to roast. At the same time, the indium was turned into the indium powder, and the pyrometallurgy could be done after that. During the process of pyrometallurgy, large amounts of oxide layer were formed and covered the indium surface. There is an equilibrium equation [27.28] between In and In_2O_3 , as follow.



The equilibrium constant K could be presented by the activities of indium, indium oxide ($a_{\text{In}_{(s)}}$, $a_{\text{In}_2\text{O}_{3(s)}}$), and the partial pressure of oxygen ($P_{\text{O}_{2(g)}}$).

By the definition of dynamic theorems, the equilibrium constant K would be introduced likes that:

$$K = \frac{a_{\text{In}_2\text{O}_{3(s)}}}{a_{\text{In}_{(s)}} \cdot (P_{\text{O}_{2(g)}})^{\frac{3}{2}}} \quad (4-2)$$

Therefore, the equilibrium partial pressure of oxygen between In and In_2O_3 could be gotten.

$$\log P_{\text{O}_{2(g)}} = \frac{-2}{3} \log K \quad (4-3)$$

In the process of pyrometallurgy, the residual elements in the sponge indium would be considered except the previous equilibrium equation (4-1) has been mentioned. There are four thermodynamic equilibrium equations about Sn/SnO₂, Al/Al₂O₃, Zn/ZnO, Mg/MgO, they would be listed at the table 4-2. And the diagrams for equilibrium partial pressure of oxygen between each metal and its oxide would be presented at figure 4-12.

Table 4-3 the oxidation reactions of each element: (included the values of ΔG)

Reaction	$\log K$	$\Delta G(kJ)$
$2\text{In}_{(s,l)} + \frac{3}{2}\text{O}_{2(g)} \rightarrow \text{In}_2\text{O}_{3(s)}$	$\log K = -\frac{3}{2} \log P_{\text{O}_{2(g)}}$ $(\log K = -17.043 + \frac{48512}{T})$	$\Delta G = -928.86 + 0.3326T$
$2\text{Al}_{(s,l)} + \frac{3}{2}\text{O}_{2(g)} \rightarrow \text{Al}_2\text{O}_{3(s)}$	$\log K = -\frac{3}{2} \log P_{\text{O}_{2(g)}}$ $(\log K = -17.29 + \frac{88395}{T})$	$\Delta G = -1692.5 + 0.33T$
$\text{Sn}_{(s,l)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{SnO}_{(s)}$	$\log K = -\frac{1}{2} \log P_{\text{O}_{2(g)}}$ $(\log K = -5.346 + \frac{15038}{T})$	$\Delta G = -287.94 + 0.102T$
$\text{Sn}_{(s,l)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{SnO}_{2(s)}$	$\log K = -\log P_{\text{O}_{2(g)}}$ $(\log K = -11.057 + \frac{30497}{T})$	$\Delta G = -583.94 + 0.211T$
$\text{Zn}_{(s,l)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{ZnO}_{(s)}$	$\log K = -\frac{1}{2} \log P_{\text{O}_{2(g)}}$ $(\log K = -5.293 + \frac{18324}{T})$	$\Delta G = -350.85 + 0.101T$

$\text{Mg}_{(s,l)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{MgO}_{(s)}$	$\log K = -\frac{1}{2} \log P_{\text{O}_{2(g)}}$ $(\log K = -5.614 + \frac{31387}{T})$	$\Delta G = -600.97 + 0.107T$
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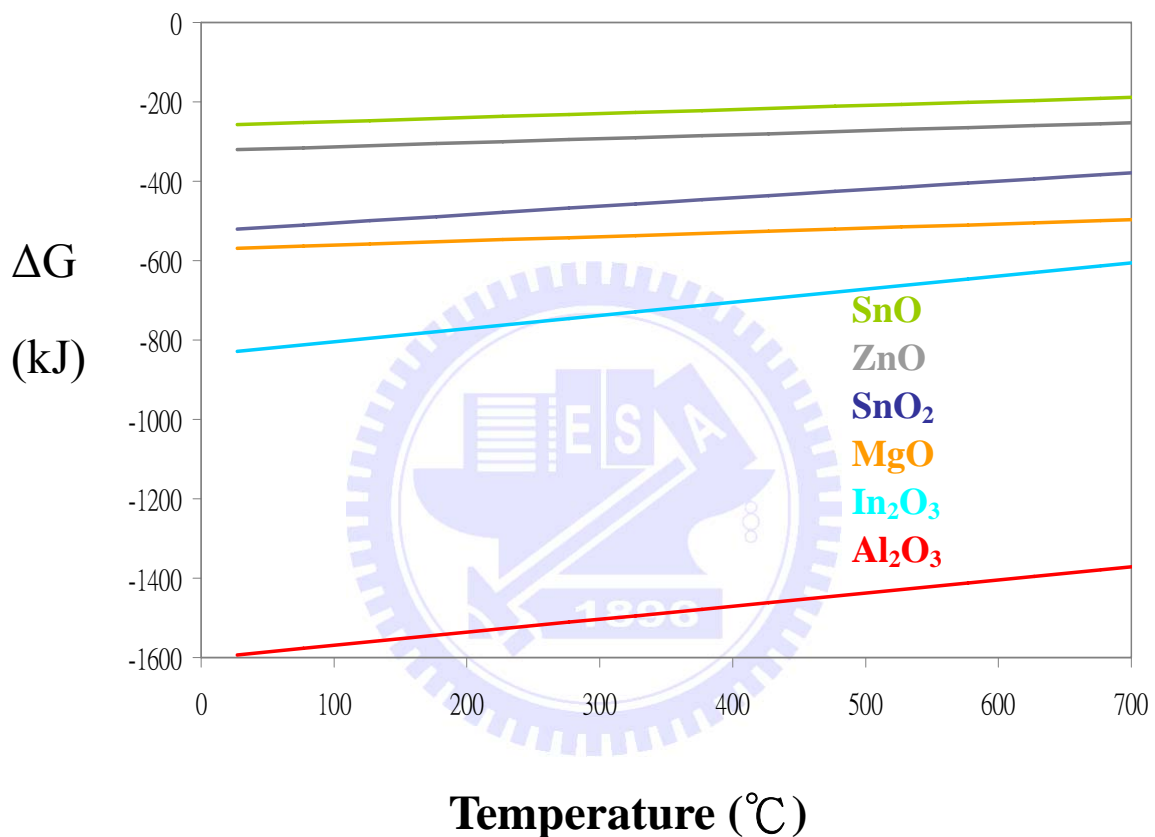
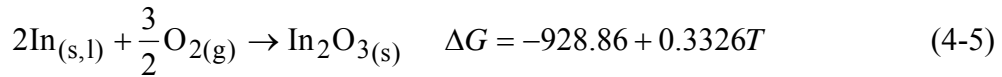
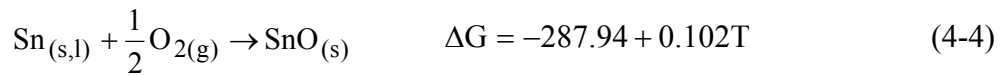


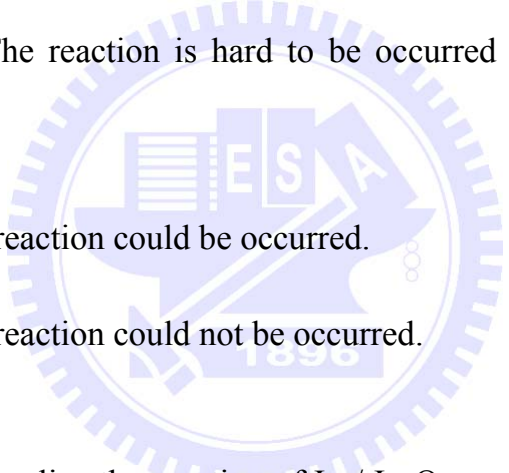
Fig.4-12 Variation of the Gibbs free energy of each element with the increase of temperature

In the figure 4-12, the possible reactions would be found easily, and it was drawn by the information of table 4-2. In order to realize the stability of the oxides, the curve provided some evidences. For example, two kinds of compounds could be created by the oxides of tin, the SnO and SnO₂. According

to the figure 4-12, the tin oxides are unstable than other elements. Then the reactions of Sn / SnO and In / In₂O₃ were listed.



The value of $\Delta G_{4.4} = -229.494$ kJ of the formula 4-4 if the temperature was 300 °C (573K). And the value of $\Delta G_{4.5} = -738.28$ kJ of the formula 4-5 at the same temperature. Evidently, the value of $\Delta G_{4.4}$ was larger than that of $\Delta G_{4.5}$, $\Delta G_{4.4} = -229.494$ kJ > $\Delta G_{4.5} = -738.28$ kJ. According to the thermodynamic theorems, the possibility of the thermodynamic reaction is depending on the values of Gibbs free energy. The reaction is hard to be occurred if the ΔG values are getting large.


 { $\Delta G < 0$, the reaction could be occurred.
 { $\Delta G > 0$, the reaction could not be occurred.

Therefore, we could realize the reaction of In / In₂O₃ was occurred easily than Sn / SnO. Equally, the order of reactions occurred was:



That is to say, the In₂O₃ could be formed before the SnO and SnO₂ were produced. Tin was doped with In₂O₃ easily because of the same atomic structures. In order to avoid the combination of Sn in the metal In, Sn would be separated out from ITO wasted solution initially. Another observation was the Al₂O₃ layers formed instantaneously and they would be extracted by slags. The phenomenon was evidently found in the ITO wasted solution or ITO wasted

mud, the Al element after hydrometallurgy was still retained in the sponge indium. After pyrometallurgy, the Al element was completely removed.

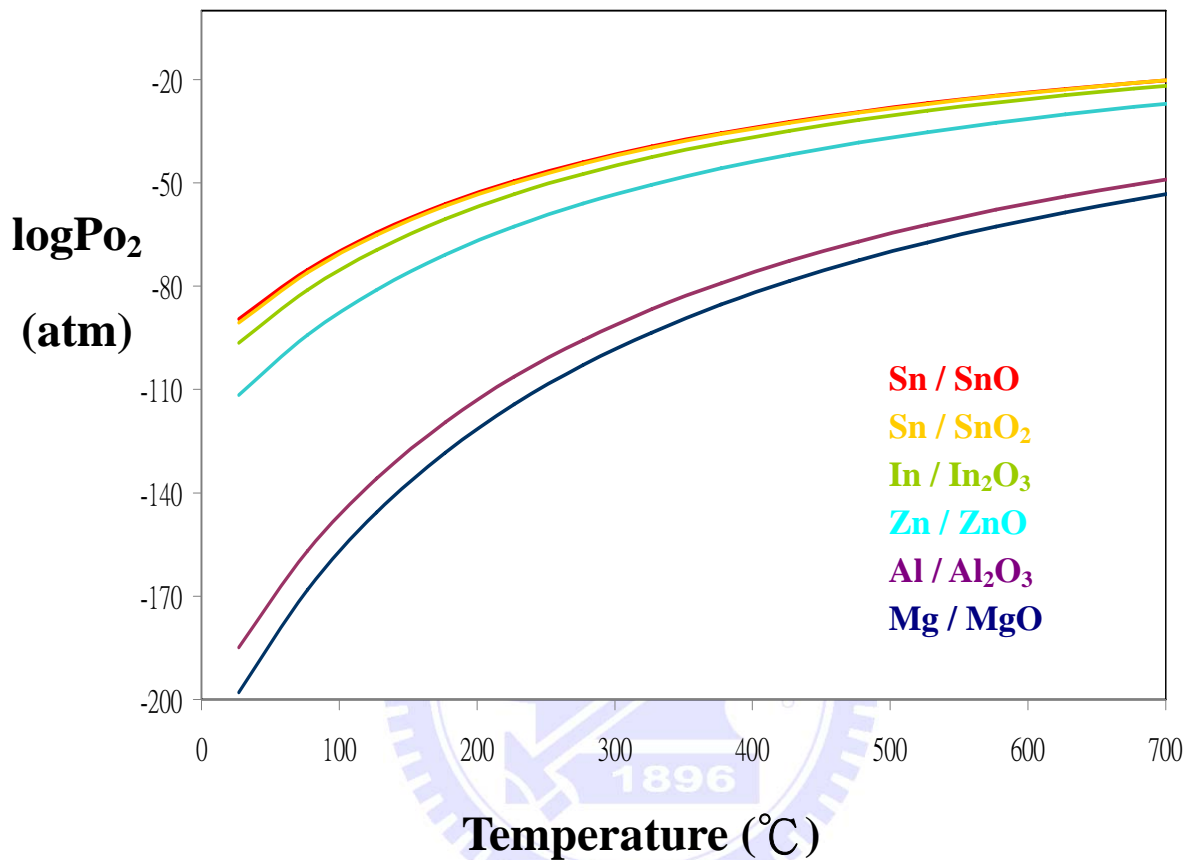


Fig. 4-13 Variation of the partial pressure of oxygen for each element with the increase of temperature

In the figure 4-13, the partial pressure of oxygen was an influent factor in the process of pyrometallurgy. From the thermodynamic calculations, the reaction of Mg/MgO was found to be the fast one occurred in the system. The MgO was easily combined with slags because of the great ability of oxidation. In addition, the first three compounds could be formed in the pyrometallurgy were Mg/MgO, Al/Al₂O₃, and Zn/ZnO. The results were used to confirm the reducing agents, Zn and Mg, and they would be eliminated with slags in the pyrometallurgy.

Table 4-4 the sublimation and evaporation of each element: (included the values of ΔG)

Reaction	$\log K$	$\Delta G(kJ)$
$\text{In}_{(s,l)} \rightarrow \text{In}_{(g)}$	$\log K = \log P_{\text{In}(g)}$ $(\log K = 5.445 - \frac{12436}{T})$	$\Delta G = 238.11 - 0.104T$
$\text{Al}_{(s,l)} \rightarrow \text{Al}_{(g)}$	$\log K = \log P_{\text{Al}(g)}$ $(\log K = 6.935 - \frac{17151.2}{T})$	$\Delta G = 328.39 - 0.132T$
$\text{Sn}_{(s,l)} \rightarrow \text{Sn}_{(g)}$	$\log K = \log P_{\text{Sn}(g)}$ $(\log K = 5.426 - \frac{15460}{T})$	$\Delta G = 296.013 - 0.104T$
$\text{Zn}_{(s,l)} \rightarrow \text{Zn}_{(g)}$	$\log K = \log P_{\text{Zn}(g)}$ $(\log K = 5.872 - \frac{6671.2}{T})$	$\Delta G = 127.73 - 0.112T$
$\text{Mg}_{(s,l)} \rightarrow \text{Mg}_{(g)}$	$\log K = \log P_{\text{Mg}(g)}$ $(\log K = 5.851 - \frac{7570.4}{T})$	$\Delta G = 144.95 - 0.112T$

In the table 4-3, the sublimation and evaporation of each element would be introduced. The figure 4-14 was drawn by the information of the table 4-3. Especially focused on the element Al, the value of $\log P_{\text{Al}(g)}$ at the temperature, 300°C (573K), was about -22.995, and the value was much smaller than other elements. From the thermodynamic theorems, the Al vapor was produced easily at the start of pyrometallurgy. In addition, the Mg vapor was produced before Zn vapor in the figure 4-14 at the same temperature. The Mg powder would be decrease efficiently in the process of pyrometallurgy. In contrary to Zn powder,

it was not easy to turn into the Zn vapor, and the more large amounts of residues were expected.

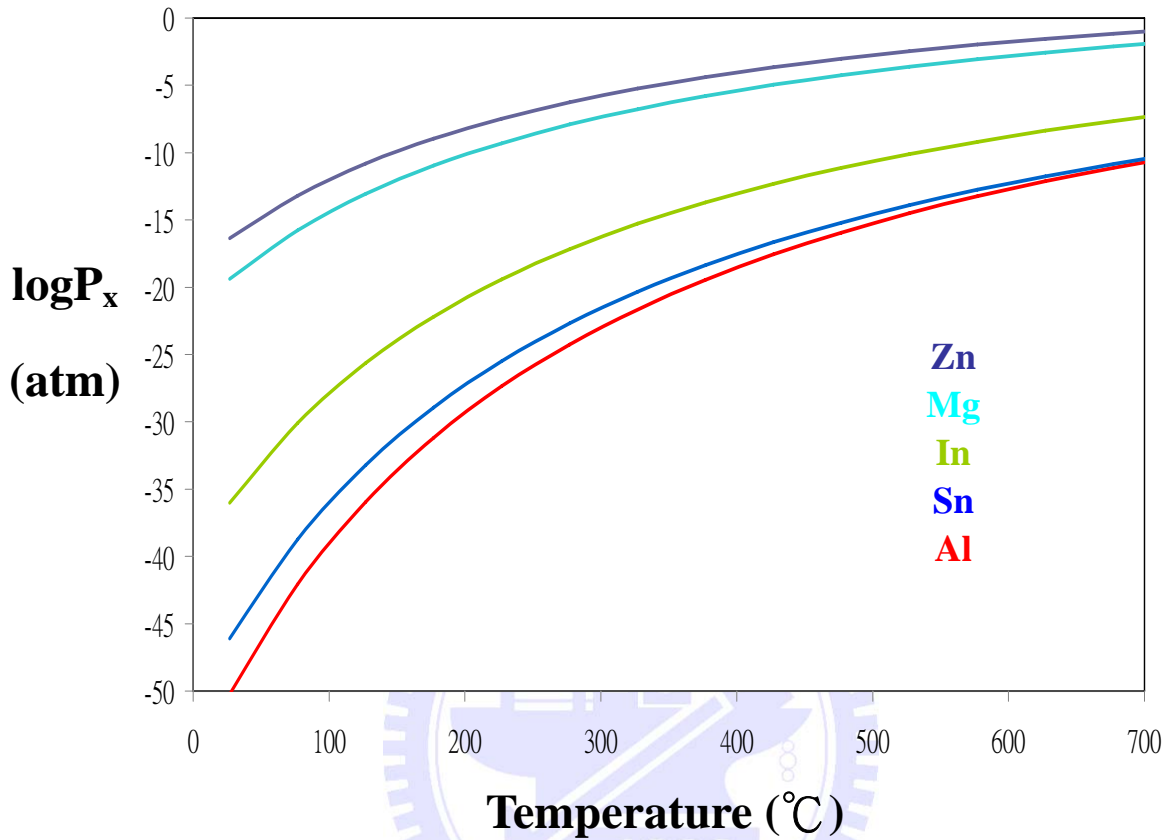


Fig.4-14 Variation of the vapor pressure of each element with the increase of temperature

4.5 The EDX and OM results of ITO wasted solution after pyrometallurgy

4.5.1 The EDX results of ITO wasted solution

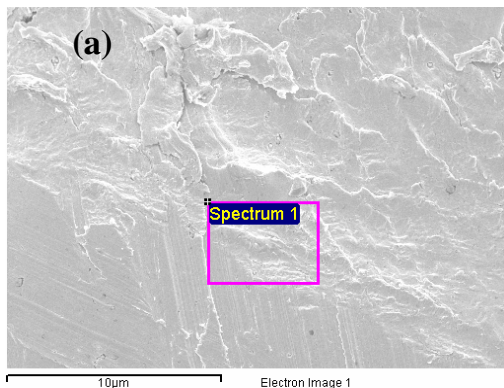


Fig. 4-15 (a)-(b) EDX results of pure indium was replaced by Zn and the slags with NaOH. (a) SEM image of pure indium. (b) Residual Sn in pure indium.

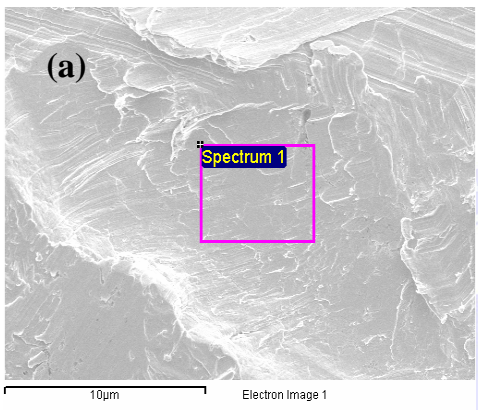
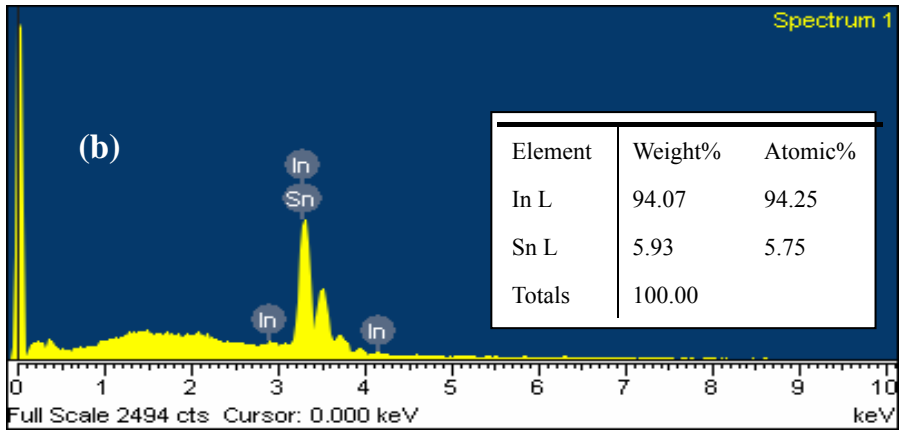
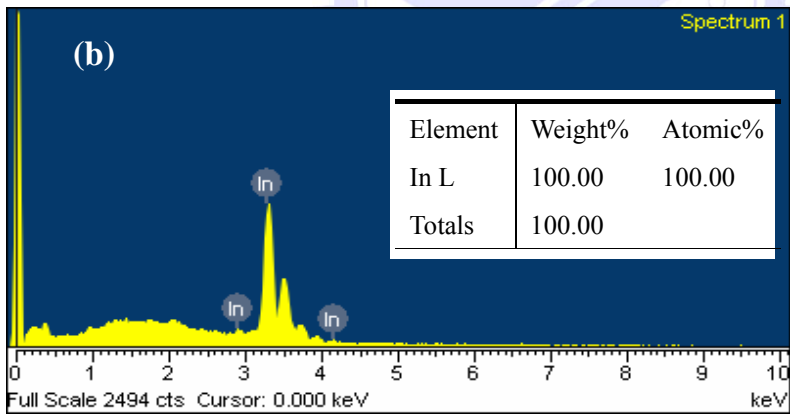


Fig. 4-16 (a)-(b) EDX results of pure indium which was replaced by Mg and the slags with NaOH. (a) SEM image of pure indium. (b) The indium with a purity of 100 %.



In the figure 4-15, the residuals of element Sn was found in recycling metal indium if we used the Zn powder as reducing agent. In contrary to the reducing agent, Mg powder, and it is useful in extracting indium. In the figure 4-16, the composition of recycling indium could reach the purity of 100 wt%. There were two kinds of layer during the process of pyrometallurgy. One was the slags, and they would be suspended on the top of the crucible. The other

was the pure indium, and it would be sunk to the bottom of the crucible. The slags with large amounts of NaOH were used to extract the impurities from the recycling indium, and they would be removed by blowing with water.

4.5.2 The OM images of ITO wasted solution

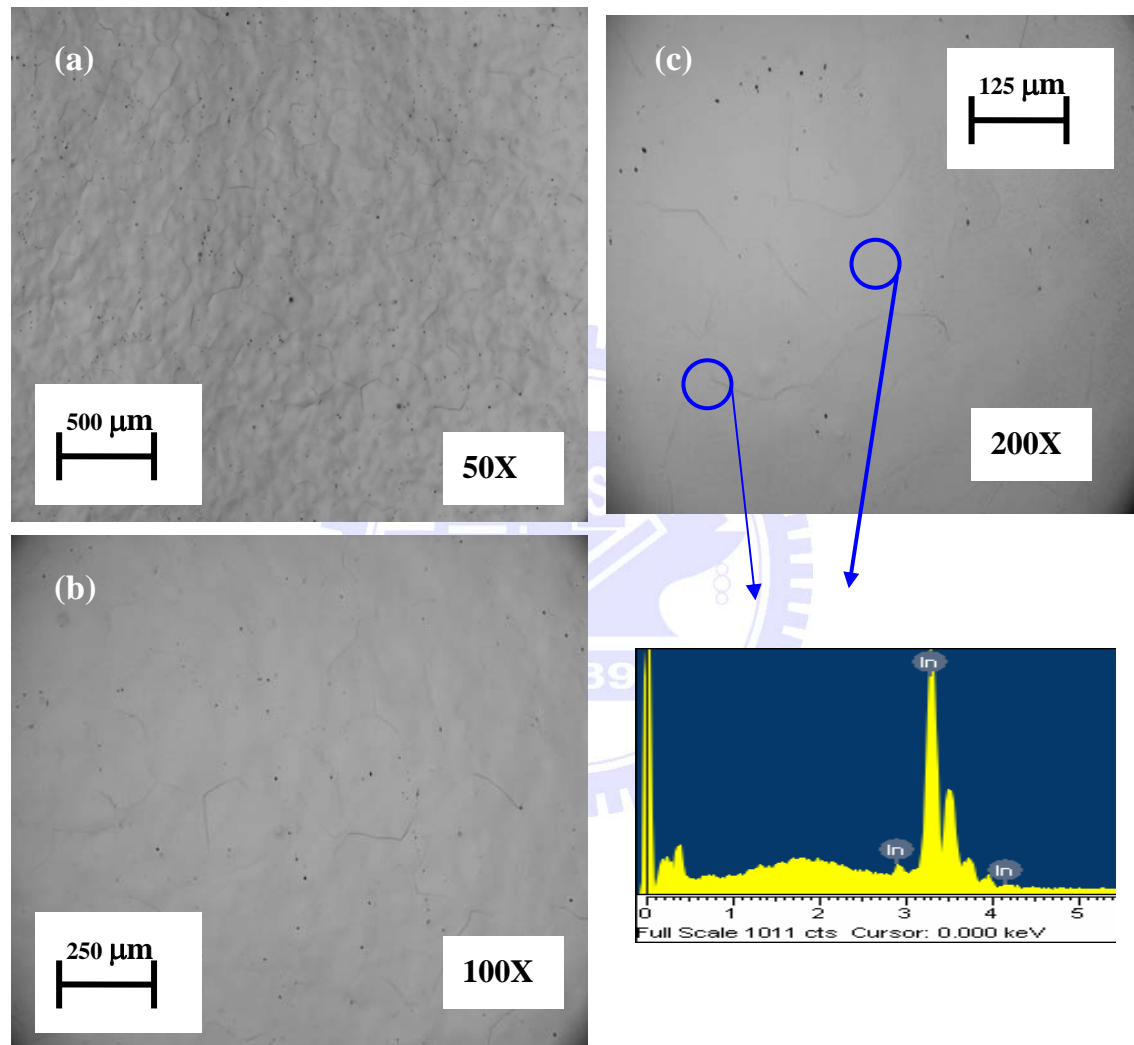


Fig. 4-17 (a)-(c) OM images of pure indium was replaced by Mg and the slags with NaOH. (a) OM image of pure indium, 50X. (b) OM image of pure indium, 100X. (c) OM image of pure indium, 200X.

From the EDX results, the composition of indium was about 100 wt%, and we usually defined the indium with a purity of 99.9wt%. The clear grain and

grainboundaries were found in the figure 4-17. Basically, the whole microstructure was smooth. The high-purity indium with a purity of 99.999 wt% was showed in the figure 4-24, and it would be the standard sample for us.

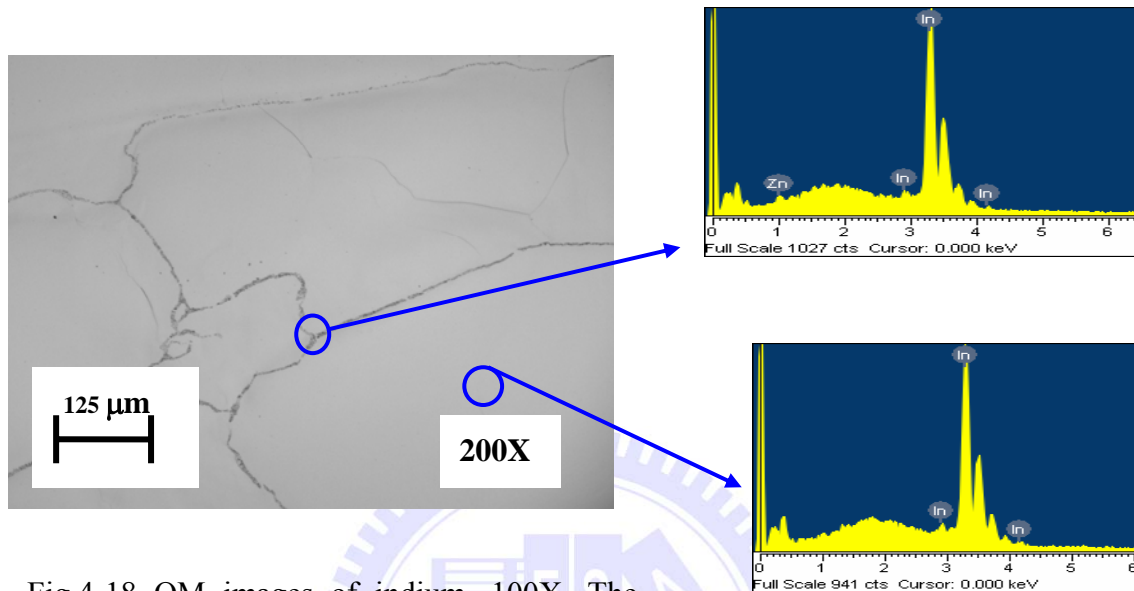


Fig.4-18 OM images of indium, 100X. The indium was replaced by Zn and the slags with NaOH.

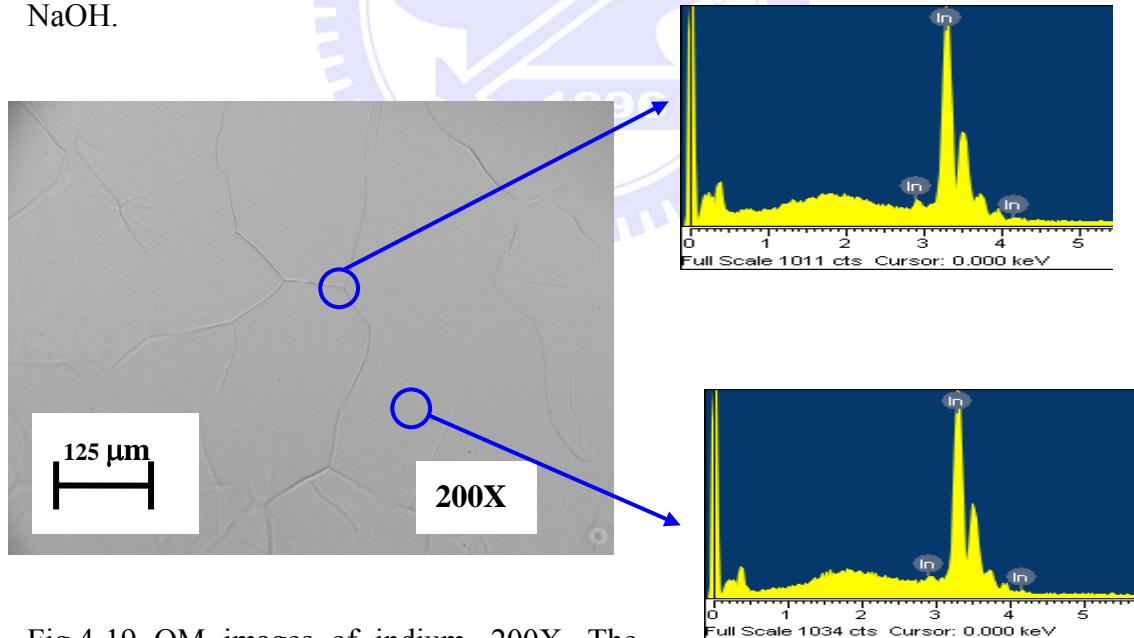


Fig.4-19 OM images of indium, 200X. The indium was replaced by Mg and the slags with NaOH.

In the 4-18 and 4-19, the comparison of different reducing agents after

pyrometallurgy was presented. From the EDX results, the Mg was the better reducing agents in recycling indium from ITO wasted solution. The NaOH was used to extract impurities from sponge indium and it was not the influent factor in the section 4.5.2.

4.6 The EDX and OM results of ITO wasted mud after pyrometallurgy

4.6.1 The EDX results of ITO wasted mud

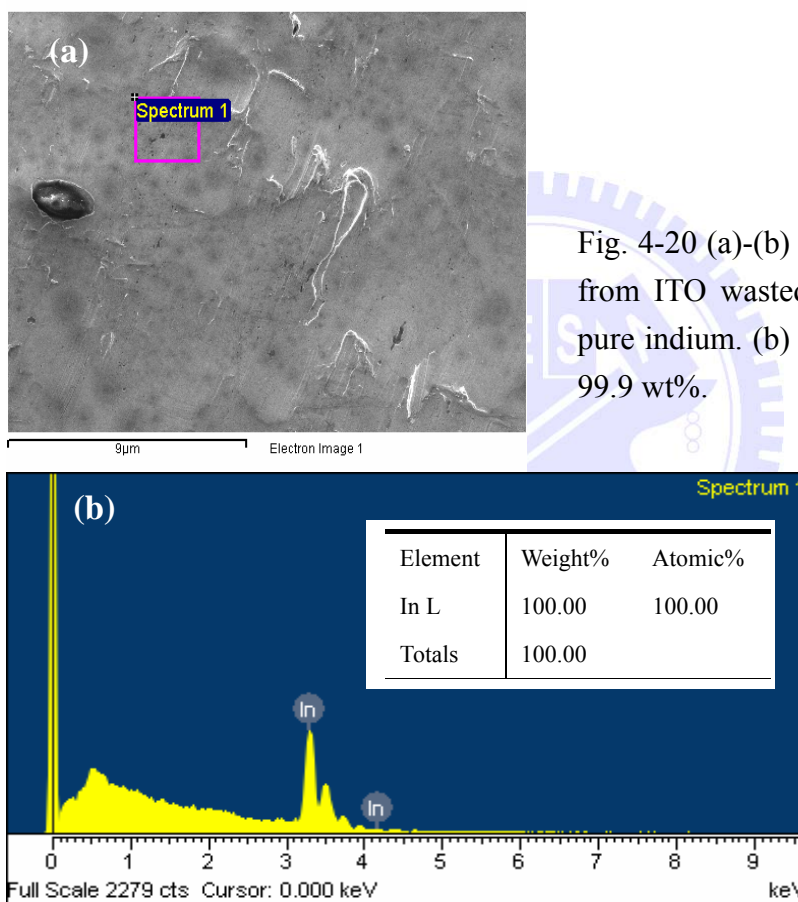


Fig. 4-20 (a)-(b) EDX results of pure indium from ITO wasted mud. (a) SEM images of pure indium. (b) The indium with a purity of 99.9 wt%.

In the figure 4-20, the EDX results were presented the indium with a purity of 99.9 wt%. The Zn powder was used to replace indium from ITO wasted mud. In contrary to the results of fig.4-10(b) and 4-11(b), the elements, such as Cr, Cl, and Al were eliminated with slags after pyrometallurgy. The KOH was used to extract impurities from sponge indium.

4.6.2 The OM images of ITO wasted mud

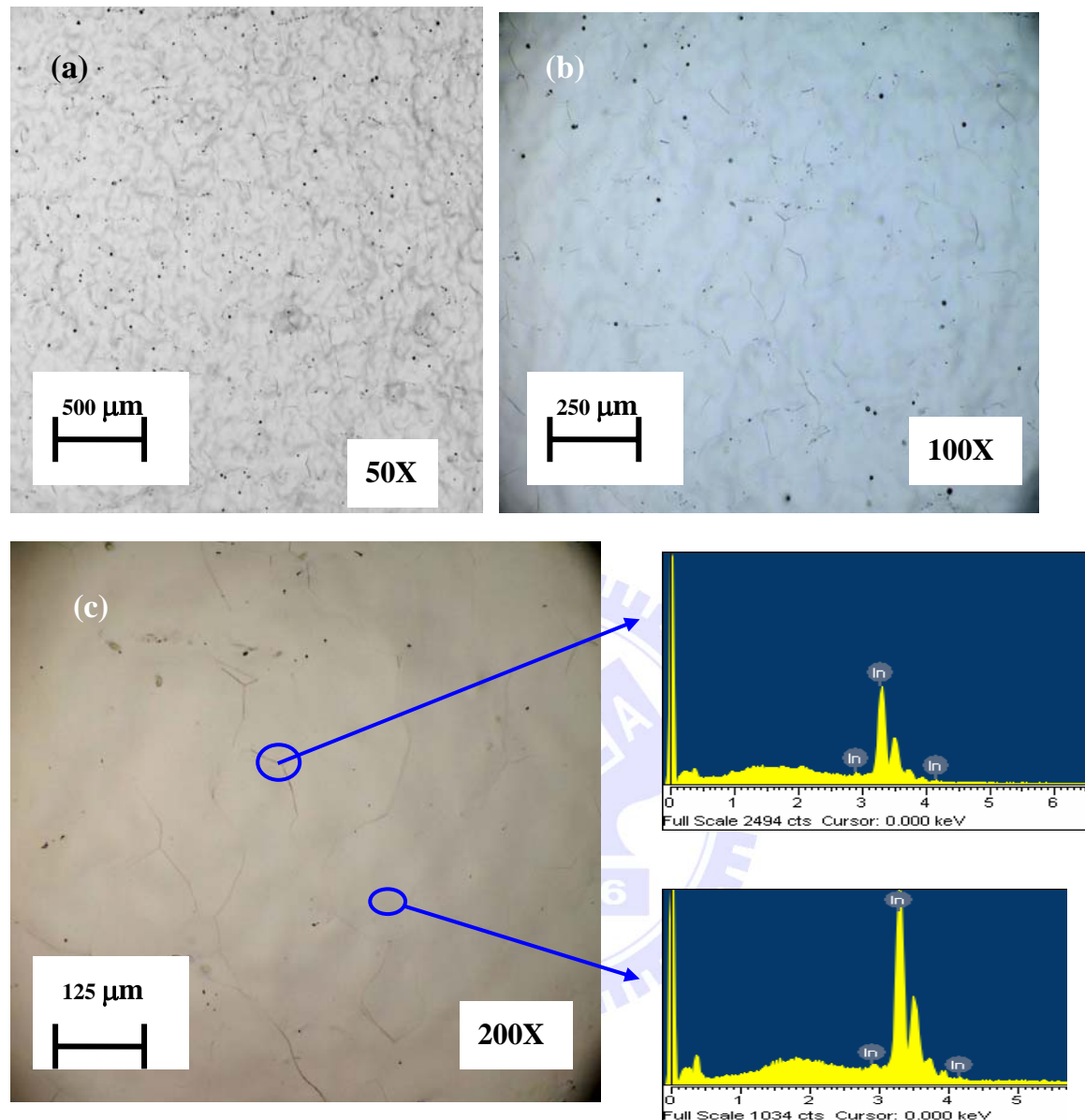


Fig. 4-21 (a)-(c) OM images of pure indium was replaced by Zn and the slags with KOH. (a)OM image of pure indium, 50X. (b) OM image of pure indium, 100X. (c) OM image of pure indium, 200X.

In the fig.4-21 (c), the purity of indium was about 99.9%. Besides, some pitting points were found in the figure 4-21(a) and (b). The reason for forming these pitting points is the electric current changes instantaneously, and it made one part of indium reactive and then the corrosion would be occurred. Basically,

the whole microstructure was smooth. The slags with KOH didn't exist in the pure indium because of the removal of slags by water.

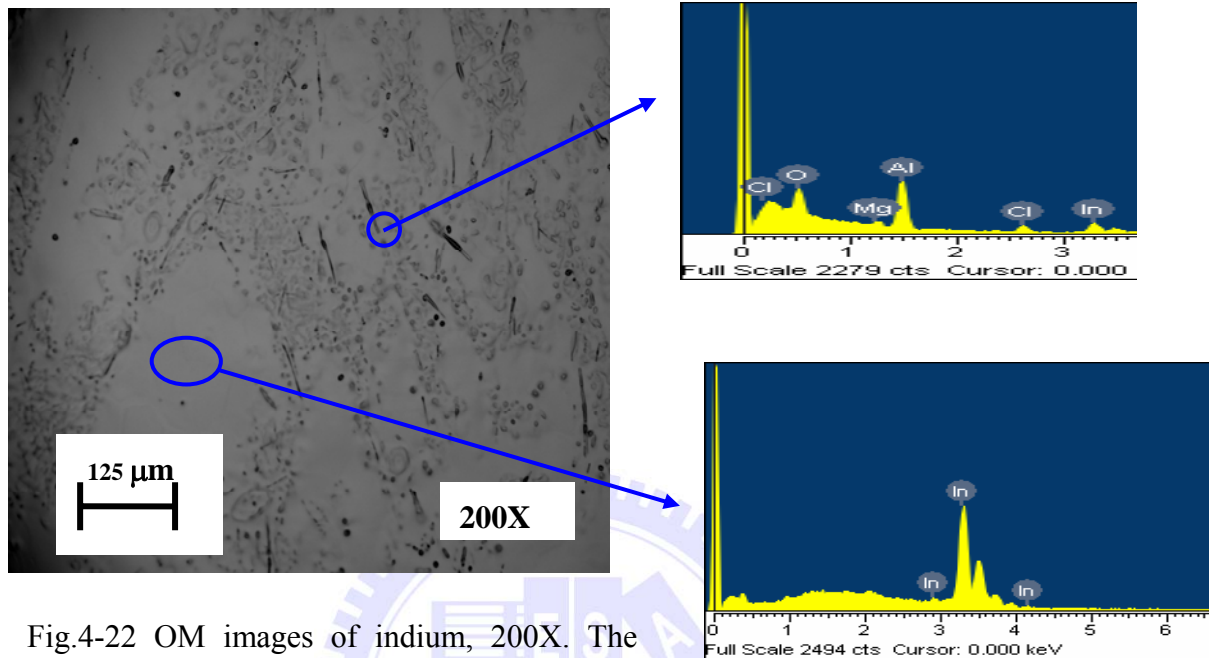


Fig.4-22 OM images of indium, 200X. The indium was replaced by Mg and the slags with KOH.

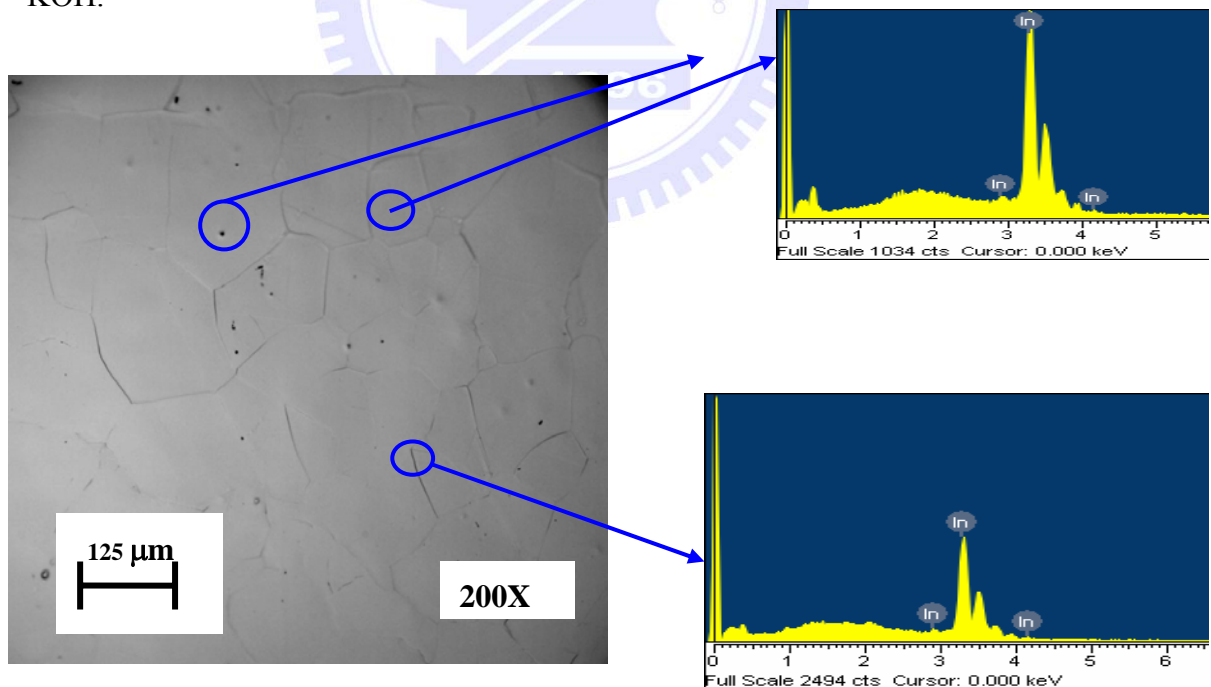


Fig.4-23 OM images of indium, 200X. The indium was replaced by Zn and the slags with KOH.

The comparison of two different reducing agents, Zn and Mg in recycling indium from ITO wasted mud. In the figure 4-22, the indium was replaced by Mg, and many impurities were retained at the grain-boundaries. From the EDX results of the impurities, the Mg was still existed at the boundaries after pyrometallurgy. On the other way, the OM image of pure indium was replaced by Zn was showed in the fig.4-23, and the microstructure was smooth. Besides the purity of indium was 99.9 wt%. Therefore, the pure indium could be replaced efficiently by Zn.

4.7 Optimized experimental conditions in the research

4.7.1 Optimized Electro-polishing Condition

Table 4-5 The condition of electro-polishing.

Metal	Temp.	Voltage	Times	solution
Indium	1 °C	15~20V	5~10 min	550ml, methanol(66.4%) 250ml, HNO ₃ (30%) 30ml, monobutylether (3.6%)

The supplement current density of electro-polishing is about 4~5 mA. During the process, the oxide layer of metal indium is the color of dark yellow. Therefore, the periods of electro-polishing depended on the luster of indium. We put the indium in the sample and continued to execute electro-polishing if the luster of indium is still yellow. The molds of electro-polishing were introduced in the section 3.2.2.

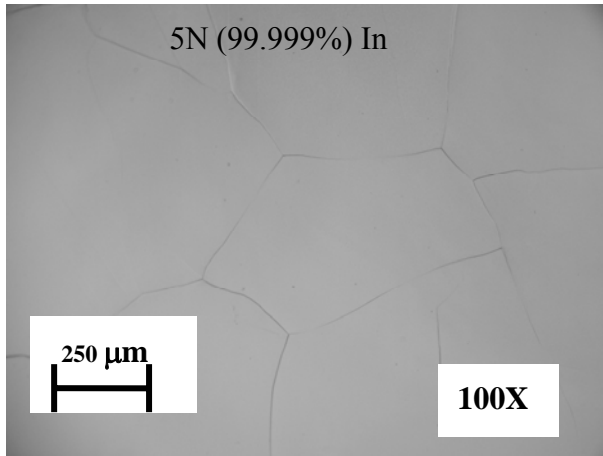


Fig. 4-24 The OM image of pure indium (99.999%)

In the fig.4-24, the OM image of indium with a purity of 5N was depicted. The standard sample was used to compare with the other OM images of indium.

4.7.2 The properties and polishing skills of indium

The skills for primary mechanical polishing to grind the indium are using fine sandpapers over the number 400. Slow and flat grabbing of the sample could reach the flat plane of the metal indium. The metal indium is so soft that we could cut straight by the scissors. After pyrometallurgy, the metal indium would be cut to a suitable shape in order to put in the molds of electro-polishing.

4.7.3 Optimized Conditions of Hydrometallurgy and Pyrometallurgy

4.7.3.1 Optimized conditions of ITO wasted solution

Two factors, such as the contents of Mg, and the contents of NaOH would be taken into accounts in recycling indium from ITO wasted solution. One is the contents of Mg; it was with great ability of oxidation, and the contents of Mg improved the amounts of In by replacement. The other is the slags with NaOH; the impurities could be extracted by them and the amounts of pure

indium were abundant by removal of slags. Therefore, the how the two factors influenced the process of recycling indium was introduced later.

Let we especially discussed the influence of temperature. If the Mg was put in the wasted solution, it would react with In^{3+} excitedly. Therefore, the temperature was raised quickly and the process of hydrometallurgy was faster. The influence of temperature was less important in recycling indium by Mg.

According to the chemical reduction theorems, the sponge indium was replaced by the equal mole of Mg in the hydrometallurgy. The amounts of sponge indium increased with the increase contents of Mg because many kinds of elements were involved in it. Until In^{3+} didn't exist in the ITO wasted solution nearly, the amounts of sponge indium were not replaced anymore. The figure 4-25 showed the relationship between the amounts of indium and the contents of Mg at room temperature.

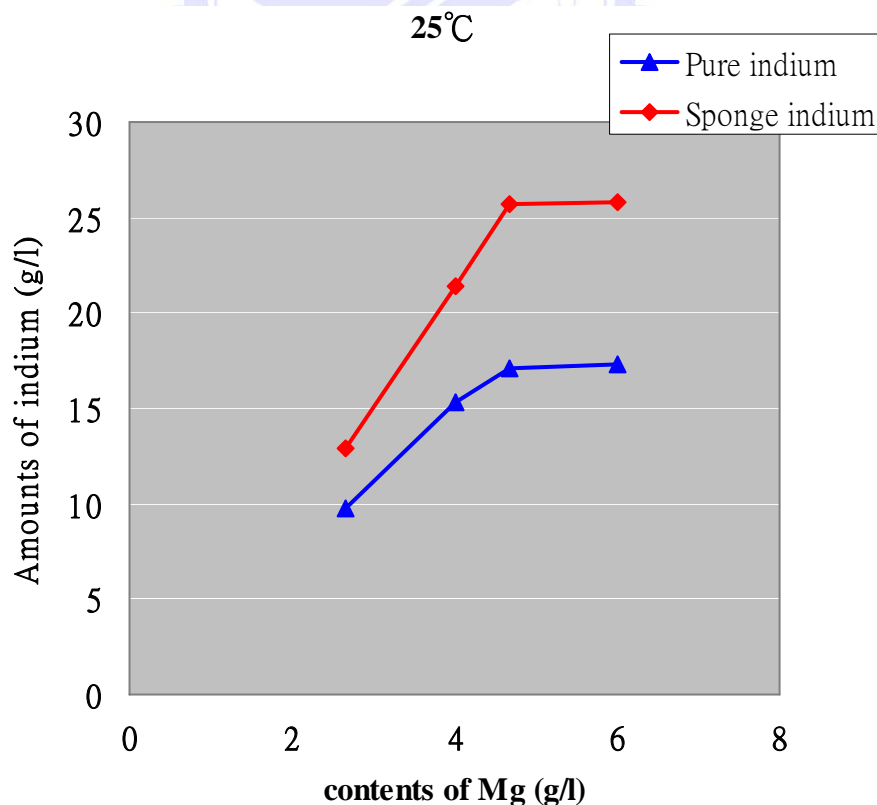


Fig. 4-25 Influence of Mg addition to the amounts of recycling indium, at 25°C

In the fig.4-25, the amounts of pure indium were found less than sponge indium. The pure indium was gotten after pyrometallurgy, and its purity was about 99.9 wt%. The amounts of pure indium were about 17.69g/L after pyrometallurgy. Besides, the amounts of sponge indium were about 25.72g/L. Therefore, the decrease percent was about 33 % by calculations after pyrometallurgy. The contents of Mg were used to replaced indium in the hydrometallurgy were about 4.67g/L.

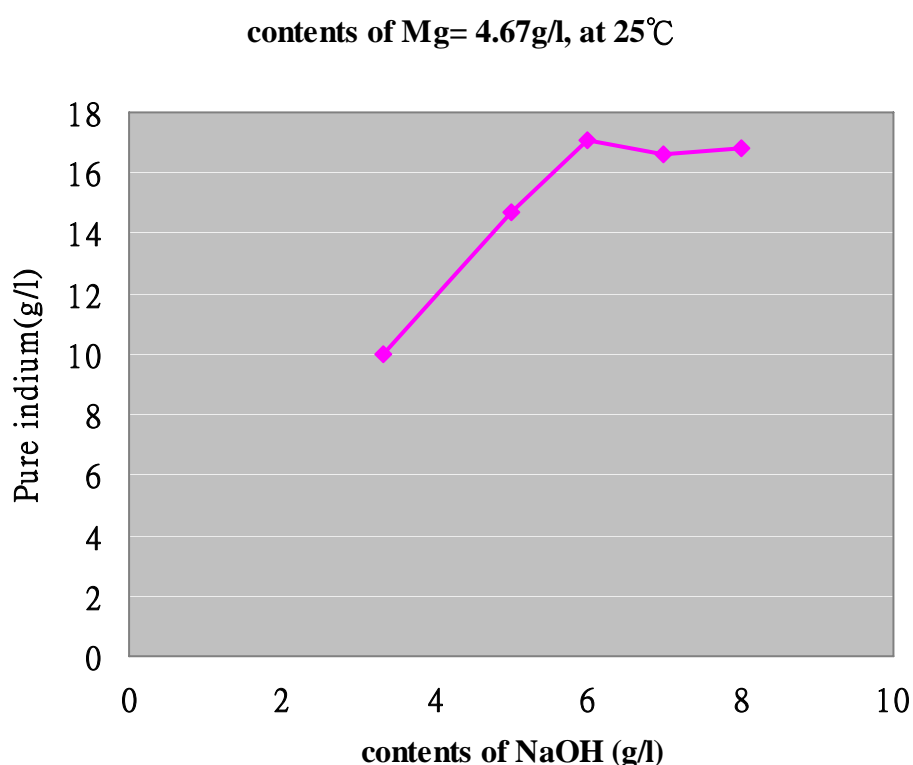


Fig. 4-26 Influence of NaOH addition to the amounts of pure indium, at 25°C

The fig.4-26 showed the influence of contents of NaOH. In the pyrometallurgy, the slags with NaOH were used to refine the sponge indium in the ITO wasted solution. The optimized contents of NaOH were 6g/L and the pure indium was gotten by a maximum value, 17.69g/L. In addition, the slags with NaOH were easy to remove by water. It is needless to use the NaOH over 6g/L because the pure indium was not gotten over 17.69g/L.

4.7.3.2 Optimized conditions of ITO wasted mud

Three factors, such as the contents of Zn, the temperature of hydrometallurgy, and the contents of KOH would be considered in recycling indium from ITO wasted mud. Because the residual of Zn was hard to remove in the pyrometallurgy, the contents of Zn were less than Mg. The figure 4-27 showed the amounts of sponge indium by different temperatures.

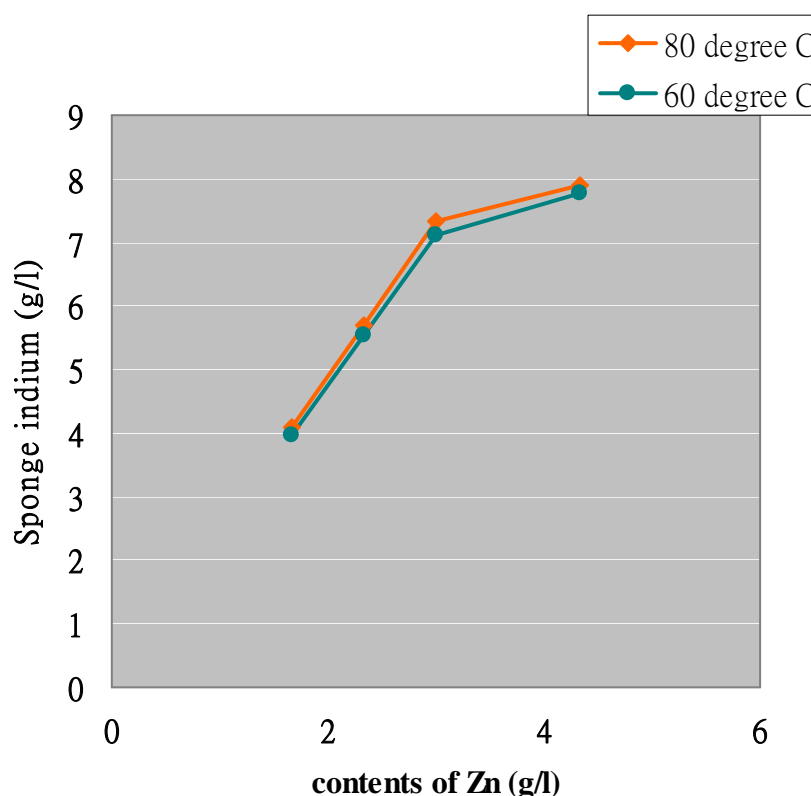


Fig.4-27 Influence of two temperatures on the amounts of sponge indium, at 60°C and 80°C

In the fig.4-27, the amounts of sponge indium were slight large at 80°C than that of 60°C. Besides the amounts of sponge indium increased with the increase contents of Zn. The fig.4-28 showed the amounts of pure indium by the temperature 60°C and 80°C. While the contents of Zn were over 3g/L, the amounts of pure indium were decrease. The changed amount of pure indium at 60°C and 80°C was about 0.53g/L, and the difference between the two temperatures was not noticeable for us. For economical reasons, we chose 60°C

as the operation temperature in the process of hydrometallurgy.

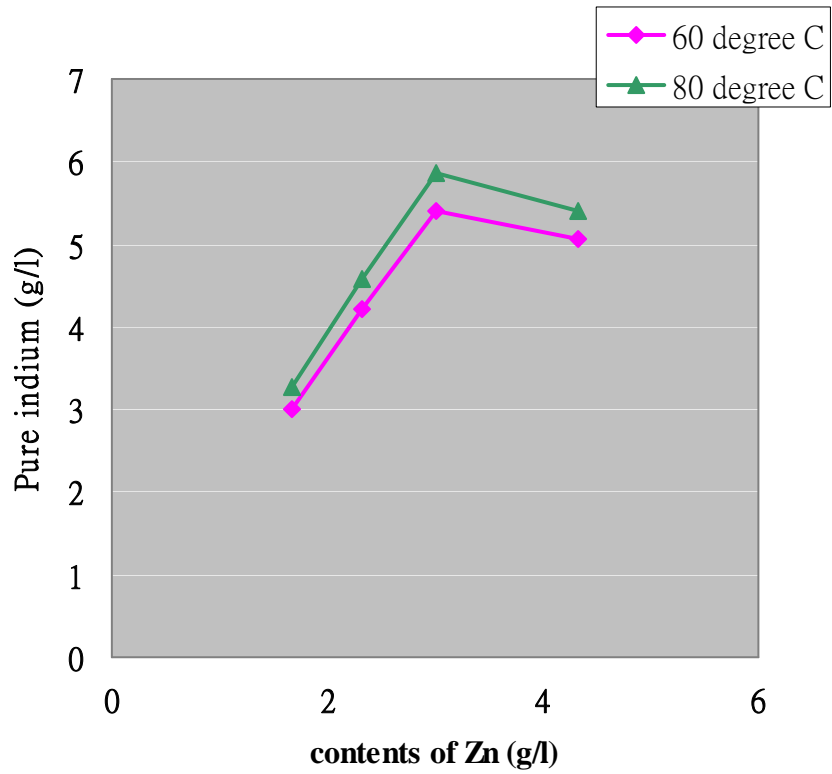


Fig.4-28 Influence of two temperatures on the amounts of pure indium, at 60°C and 80°C

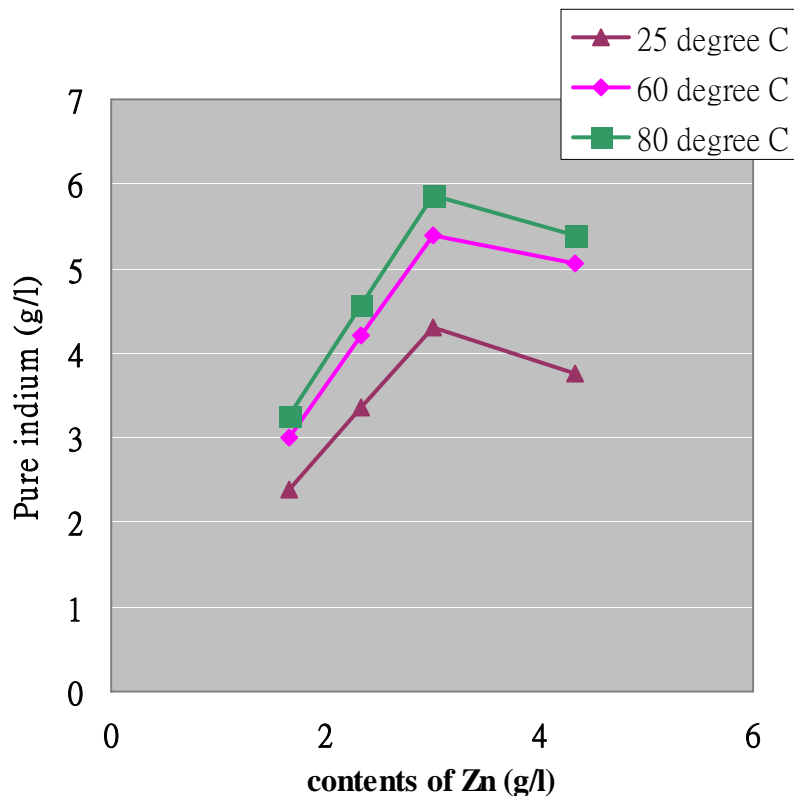


Fig.4-29 Influence of three temperatures on the amounts of pure indium, at 25°C, 60°C, and 80°C

In the fig.4-29, the influence for amounts of pure indium at three different temperatures was shown. At 25°C, the amounts of pure indium were gotten least among the three temperatures. The result pointed out the pure indium was not replaced sufficiently at low temperature. The optimized contents of Zn were 3g/L and optimized amounts of pure indium were 5.39g/L.

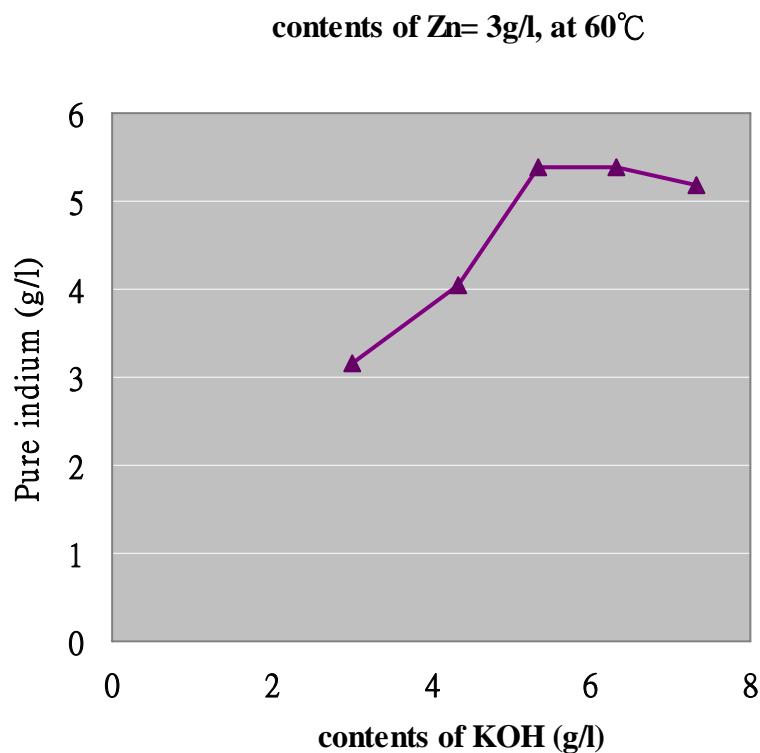


Fig. 4-30 Influence of KOH addition to the amounts of pure indium, at 60°C

The influence of contents of KOH was shown in the fig.4-30. In the pyrometallurgy, the slags with KOH were used to refine the sponge indium in the ITO wasted mud. If the contents of KOH were over 5.33g/L, the amounts of pure indium didn't increase anymore. The optimized contents of KOH were 5.33g/L and the pure indium was gotten by a maximum value, 5.39g/L.

4.7.4 The Work Window in the research

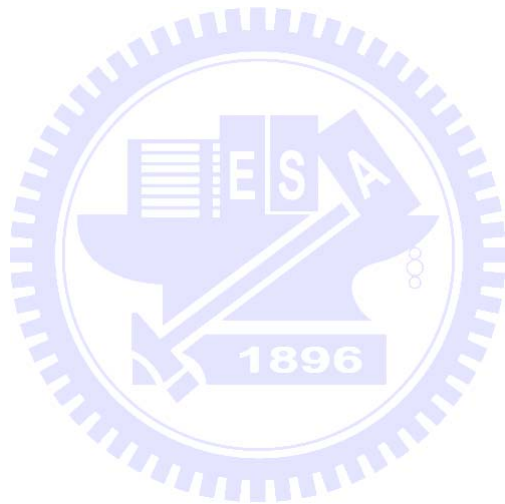
Summary of the optimized conditions was showed as follow. In the table 4-5, the optimized conditions of hydrometallurgy were the contents of Mg, the contents of Zn, and the operation temperature. In the table 4-6, the optimized conditions of pyrometallurgy were the contents of NaOH and KOH in the crucible. Finally, the decrease percent of indium was calculated.

Table 4-6 The optimized conditions of hydrometallurgy

Condition	ITO wasted materials	
	ITO wasted solution	ITO wasted mud
Contents of Mg	4.67g/L	
Contents of Zn		3g/L
Temperature	25°C	60°C
Amounts of sponge indium	25.72g/L	7.1g/L

Table 4-7 The optimized conditions of pyrometallurgy

Condition	ITO wasted materials	
	ITO wasted solution	ITO wasted mud
Contents of NaOH	6g/L	
Contents of KOH		5.33g/L
Amounts of pure indium	17.69g/L	5.39g/L
Decrease percent of indium	33 %	24 %



Chapter 5

Conclusions

1. Hydrometallurgy method was used to replace the In^{3+} from ITO wasted solution and the raw metal indium (sponge indium) was obtained a purity of 2N by the results of EDX.
2. In the hydrometallurgy, the Zn and Mg powder were used to be the reducing agents. Mg powder was better to use in the ITO wasted solution and the sponge indium was gained about 25.72g/L. Zn powder was better to use in the ITO wasted mud and the sponge indium was gained about 7.1g/L.
3. After pyrometallurgy, the decrease percent of indium was 33% in the ITO wasted solution, and the decrease percent of indium was 24% in the ITO wasted mud.
4. In recycling indium from the ITO wasted solution, the addition of Mg was 4.67g/L to replace the sponge indium at room temperature. Besides the addition of NaOH was 6g/L to make the slags. The pure indium was obtained about 17.69g/L with a purity of 3N.
5. In recycling indium from the ITO wasted mud, the addition of Zn was 3g/L to replace the sponge indium at 60°C. Moreover, the addition of KOH was 5.33g/L to make the slags. The pure indium was obtained about 5.39g/L with a purity of 99.7%.

Chapter 6

Future works

1. The purity of indium was improved by the method of electrolysis. By controlling the proper concentrations of electrolyte and the current density, the high-purity indium would be obtained.
2. In the future, we expected the indium with a purity of 5N by the methods of pyrometallurgy and electrolysis.



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