PRODUCTION OF Al-Cu-Zn ALLOYS FOR THE METHANOL SYNTHESIS REACTION

A DISSERTATION

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requirements for the award of the degree
of
MASTER OF ENGINEERING
in
METALLURGICAL ENGINEERING
(INDUSTRIAL METALLURGY)

By

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled 'PRODUCTION OF Al-Cu-Zn ALLOYS FOR THE METHANOL SYNTHESIS REACTION' in partial fulfilment of the requirement for the award of the Degree of Masters of Engineering submitted in the Department of Metallurgical Engineering of the University is an authentic record of my own work carried out during a period from May,1990 to Feb. 1991 under the supervision of Dr.(Mrs.) V. Agarwala, Lecturer Met. Engg. and Dr. A.K. Agarwal, Lecturer, Chemical Engineering Department.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

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Candidate's Signature

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

The Catalytic conversion of synthesis gas (a mixture of $CO_2/CO/H_2$) to methanol is an important industrial process. The zinc promoted Raney Copper catalyst produced by partial leaching was found to produce yields of methanol double to that obtained on a commercial catalyst. The importance of methanol as a clean synthetic fuel and chemical feedstock has led to wide spread interest in improving economics of production.

In this investigation Al-33.1 wt% Cu-17.6 wt% Zn and Al-32.4 wt% Cu-9.3 wt% Zn alloys were prepared and subjected for leaching at various temperatures (30,40 and 50°c) and different aqueous sodium hydroxide concentration (20 , 30 and 40 wt%) at a constant time of one hour. The leaching mechanism in the above alloy systems are studied with the help of Scanning Electron Microscope (SEM), X-ray diffraction studies and Electron Probe Micro Analysis (EPMA).

It is observed from the X-ray analyses and Micro Probe results that the two phases $CuAl_2$ and solid solution of Aluminium are present in the as-cast alloys, whereas in leached alloy Cu and Cu_2O phases are present in the alloy. Coring effect has been observed in the solid solution of Aluminium containing Copper and Zinc.

For both alloys, the leached thickness increased with increase in temperature and sodium hydroxide concentration.

While leaching, solid solution of Aluminium is leached out. This is due to the electrode potential difference developed between the two phases. These two phases are electrically short circuited through the body of the alloy. As soon as the alloy is in contact with the aqueous sodium hydroxide solution, local cell action takes place and dissolution takes place at anode.

It is observed from the Electron Probe Microscopic Analysis, that the concentration of Aluminium and Zinc decreased uniformly in the leached region, where as the amount of Copper is proportionally high. It is also observed that Aluminium is leached out from $CuAl_2$ phase.

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CONTENTS

CHAPTER — 1

INTRODUCTION

The catalytic conversion of synthesis gas (a mixture of $CO_2/CO/H_2$) to methanol is an important industrial process. The chief commercial uses of methanol are in the manufacture of formaldehyde and acetic acid. The methanol is also used in the synthesis of many chemicals such as methylamines, dimethylterephthalate, methyl halidas etc. The importance of methanol as a clean synthetic fuel and chemical feedstock has led to widespread interest in improving the economics of production (Friedrich et al, 1982).

The modern low pressure (20-100 atm) methanol synthesis catalysts are usually based on $Cu-ZnO/Cr_2O_3$ or $Cu-ZnO/Al_2O_3$ compositions. These mixed oxide catalysts, produced by co-precipitation methods have been studied by Herman et al, 1979 and have been found to be considerably more active than separate catalytically active components.

Further improvements in methanol production could be made by the development of catalysts that have higher intrinsic activity, selectivity, thermal stability and resistance to poisoning (Marseden et al, 1980). The zinc promoted Raney copper catalyst produced by partial leaching was found to produce yields of methanol double to that obtained on a commercial copper based catalyst (Friedrich et al,1982). The most active catalyst was produced by extracting an alloy of composition 50 wt% Al, 30-36 wt% Cu and 14-20 wt% Zn with aqueous sodium hydroxide at 50°c. Friedrich et al have suggested that the level and distribution of zinc within the resultant catalyst may also be controlled and as a result the catalytic activity of these Raney catalysts may be improved.The most active component for these Raney catalysts was found to be copper. The residual zinc in the Raney catalyst was found not only to increase catalytic activity but also to extend catalyst life (Friedrich et al,1983). 50 wt% Aluminium was used since it corresponds to the composition $CuAl_2$ which is a leachable phase in Copper-Aluminium alloy used to produce Raney copper (Nadirov et al,1977).

Little is known about the structure and properties of Raney catalysts prepared from Al-Cu-Zn alloys, although these catalysts have activities comparable to those of commercial catalysts.

So in this investigation Al-32.4 wt% Cu-9.3 wt% Zn and Al-33.1 wt% Cu-17.6 wt% Zn alloys were prepared and subjected for leaching at various temperatures (30,40 and 50°c) and different aqueous sodium hydroxide concentrations

(20,30 and 40 wt%) at a constant leaching time of one hour. The leaching mechanism in the above alloy systems are studied with the help of Scanning Electron Microscope (SEM), X-ray diffraction studies and Electron Probe Micro Analysis (EPMA).

CHAPTER- 2

LITERATURE SURVEY

2.1 METHANOL SYNTHESIS:

The catalytic conversion of synthesis gas (a mixure of $CO/CO_2/H_2$) to methanol is represented by the following equations,

$$CO + 2H_2 \longrightarrow CH_3OH$$

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

The above reactions will operate at high pressure and temperatures. The reaction rate is faster in the presence of catalyst. The main sources from which synthesis gas is produced are natural gas and gassification of coal. The synthesis gas from natural gas is produced by steam reforming of methane (Chinchen et al, 1990).

2.1.1 DESCRIPTION OF METHANOL SYNTHESIS:

A typical flowsheet for the manufacture of methanol is shown in Fig. 2.1. The compressed synthesis gas is mixed initially with recycle gas in a vessel, which simultanously serves to remove any entrained oil and water. The gas stream then enters the converter (see Fig. 2.2), and by the manupulation of a by-pass valve, is directed entirely or partially through an exchanger prior to contacting the catalyst bed; this gives a close control of temperature. The

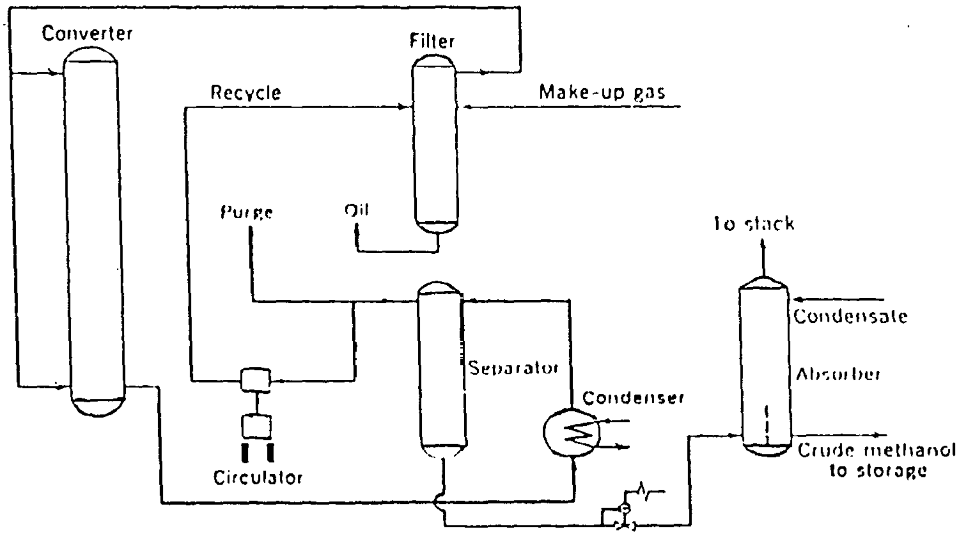


Fig 2.1 Schematic flow diagram for medium-pressure methanol synthesis.

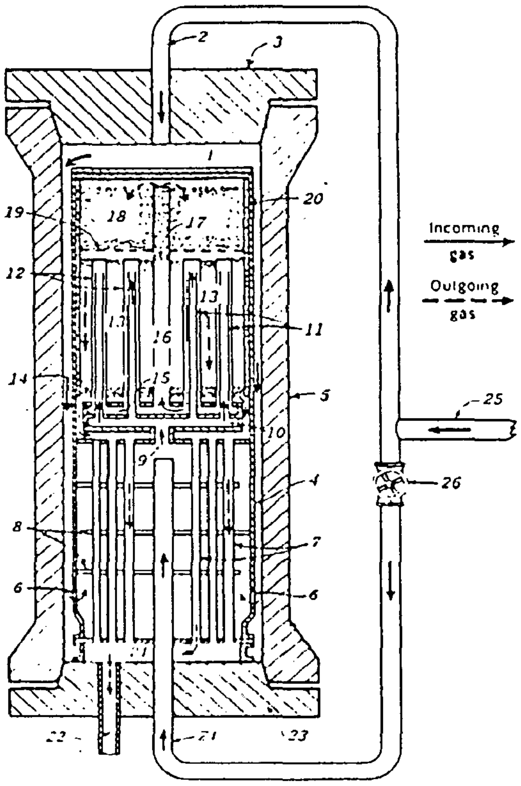


Fig.2·2 Converter 1, converter; 2, gas inlet pipe; 3, converter head; 4, heat exchanger; 5, pressure-sustaining walls; 6, openings through which gas enters exchanger; 7, heat exchanger tubes; 8, baffles; 9, port; 10, chamber; 11, tubes; 12, pipes containing tubes; 13, lower catalyst portion; 14, grate; 15, chamber superimposed above chamber 10; 16, center pipe; 17, perforated plate; 18, upper catalyst portion; 19, perforated plate; 20, insulation; 21, chamber in which reacted mixture collects; 22, outlet; 23, bottom of converter; 24, by-pass pipe; 25, main reaction gas pipe; 26, control valve.

rate of gas streams vary from plant to plant. The gaseous mixture leaving the converter passes through a separator, usually provided with a buffle arrangement. Methanol condensate is collected, a measured amount of gas is purged and the main stream enters the suction side of a circulating compressor, in which it is brought up to a pressure, and mixed with the make up gas in the filter. The methanol condensate is let down from synthesis pressure into an obsorption vessel, where dissolved gases are flashed upward and pass countercurrently against a small stream of water which returns the evaporated methanol, allowing the noncondensable gases to pass out of the system. (Anthony Standen, editor. 1967).

2.2 METHANOL SYNTHESIS CATALYST:

Methanol synthesis catalyst should have higher intrinsic activity, selectivity, thermal stability and resistance to poisoning (Marsden et al,1981). It should suppress the side reactions and promote the main reaction at as low a temperature as possible. These catalysts should also fulfil the usual requirements of chemical durability, mechanical and physical strength, relative ease of manufacture etc. (Anthony Standen, editor 1967).

In 1967 the I.C.I introduced Copper-Zinc-Chromium oxide catalyst, which is produced by co-precipitation method (Davies et al 1967). The most recent patents substitute alumina for chromia in order to achieve greater thermal stability (Casey et al 1974). Recently a range of metals comprised the third component added to support Copper-Zinc catalysts by co-precipitation method. Magnesium gave the highest activity, while vanadium appeared to give more active catalysts than chromium and aluminium. Recently some precious metals such as palladium and rhodium also gave significant yields. But non of these catalysts has yet a good enough selectivity for industrial use.

Intermetallic compounds based on copper and thorium or rare earth metals gave significant yields or exposure to synthesis gas (Chin Chen et al 1988).

Recently, Wainwright and co-workers prepared the catalysts by extraction of aluminium and zinc from Al-Cu-Zn alloys with aqueous sodium hydroxide. These zinc promoted Raney catalysts have shown high activity and selectivity (Narsden et al 1980). The active component of these Raney catalysts was found to be copper. The residual zinc in the Raney catalyst was found not only to increase catalytic activity but also to extend catalyst life (Friedrich et al 1983). Zinc oxide helps in formation of precursors in catalyst so as to give a catalyst with a high surface area of copper metal. The main function of zinc and aluminium oxides are to prevent sintering of copper crystallites. Zinc oxide also acts as scavenger of sulfur poisons.

The Raney Copper-Zinc Catalysts are also used for the reduction of Furfural to Sylvan, and recommended as the most effective catalysts one which had an initial alloy composition of 33 wt % Cu, 50 wt % Al and 17 wt % Zn (Sultanov et al, 1959). The methanol synthesis catalysts containing upto three metal oxides are used to produce higher alcohols.

2.3 CATALYST PREPARATION

Two methods, in general, are adopted to prepare the methanol synthesis catalyst, namely, co-precipitation and alloying. In co-precipitation method the catalysts are prepared by precipitating nitrates of Copper, Zinc and Alumunium/Chromium with an alkali carbonate, followed by calcination to the oxides.(Herman et al,1979, Kin´ya et al,1978).Recently,the alloy catalysts are prepared by the removal of aluminium and zinc from Al-Cu-Zn alloy with an aqueous sodium hydroxide solution as a leachant. (Marsden et al 1981, Fridrich et al, 1982,1983). Wainwright and co-workers has observed that the powdered catalysts are found unsuitable for the use in fixed bed reactors. Due to this reason the Raney copper catalyst are further prepared in to cylendrical pellets (Curry-Hyde et al, 1987). Different alloy compositions of Al-Cu-Zn alloy catalyst have been used and the ternary equilibrium diagram (Fig. 2.3) shows the alloy composition so far investigated (Bridgewater et al, 1983).

2.4 LEACHING

Leaching can be defined as the dissolution of a component from an alloy to leave behind a spongy material by corrosion process. Dezincification of brass is possibly the best known example (Fredrich et al 1981). Two mechanisms have been suggested for the process in binary alloys. In the first, it is supposed that the simultaneous dissolution of both constituents is followed by reprecipitation of the less reactive metal. The difficulty with this mechanism is that mass transfer is required from a source of low activity, the alloy, to a region of high activity, the pure metal. Alternatively, it is suggested that the more reactive constituent is selectively removed leaving an accumulation of the less reactive metal at the alloy surface. For this mechanism to be available, diffusion with in the alloy must be sufficiently fast to support the leaching process (Feller 1968).

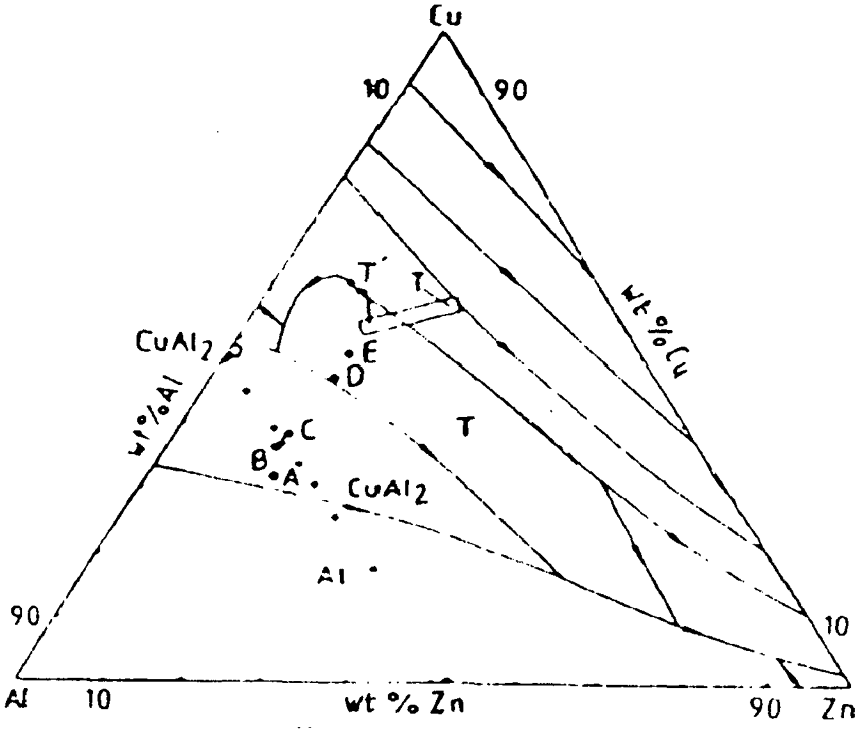


Fig. 2.3 Al-Cu-Zn phase diagram, liquidus projection, Alloys so far investigated.

The rate with which the removal of zinc and aluminium takes place in the Raney catalysts of Al-Cu-Zn alloy depends on temperature of leaching, concentration of leachant used, leaching time and the alloy composition .Tomsett et al have studied the leaching kinetics of a Cu- 50wt% Al alloy in 20wt% aqueous NaOH solution at the temperature range of 5 to 70°c. It is seen that leached depth increases with an increase in temperature. Raney catalysts were produced by alkali leaching cylendrical pellets of a Cu-39wt% Al-17.8wt% Zn alloy using a temperature range 1 to 50°c. Solution temperature dependance with the leached thickness has been observed by Curry-Hyde et al, 1987. These investigators have also studied the effect of sodium hydroxide concentration (ranging from 5 to 20wt%) on the leached depth. It is seen that leached depth increases with an increase in concentration of sodium hydroxide . Friedrich et al have studied the leaching behaviour in aqueous NaOH of Al-Cu-Zn alloys containing 50wt% Al has been interpreted in terms of alloy phase constitution. Alloys containing approximately 0,5,10,17,28,33 wt% Zn having quenched structures, have been studied. They concluded that in the low zinc alloys the preservation of the alloy microstructure in the leached product suggests strongly that the reaction of the Cu(Zn)Al_2 grains proceeds via a selective dissolution process rather than a dissolution- reprecipitation process. The later mechanism has been suggested to operate under some circumstances in the dezincification of brass.

CHAPTER- 3

EXPERIMENTAL PROCEDURE

The chapter -3 deals with the methods followed in casting of alloys, prepartion of specimens, leaching procedure and various analyses done and the details are given in the following sections.

3.1 PREPARATION OF ALLOYS

Prepartion of Al-Cu-Zn alloys were carried out in Muffle furnace. The required amounts of commercially pure Aluminium (99.5%), Copper (99.9%) and Zinc (99.5%) were taken from the ingots. The pieces of suitable sizes were weighed according to their required weight percent of the alloys. Table 3.1 shows the compositions of different alloys prepared. These elements were charged in the furnace and the homogenous melts were cast into the mild steel moulds to form ingots of size 20x20x250 mm^3.

Vertical Muffle furnace used for alloy production has an heating space of 250x250x600 mm^3. Muffle furnace was placed in a mild steel shell of size 750x750x800 mm^3. Chromel-alumel thermocouple was inserted into the furnace to measure the temperature of the furnace. Graphite crucible with a height of 150 mm and top diameter 110 mm was used for able 3.1 Composition of alloys

	ALLOY A	ALLOY B
ALUMINIUM	50 wt%	55 wt%
COPPER	35 wt%	35 wt%
ZINC	15 wt%	10 wt%

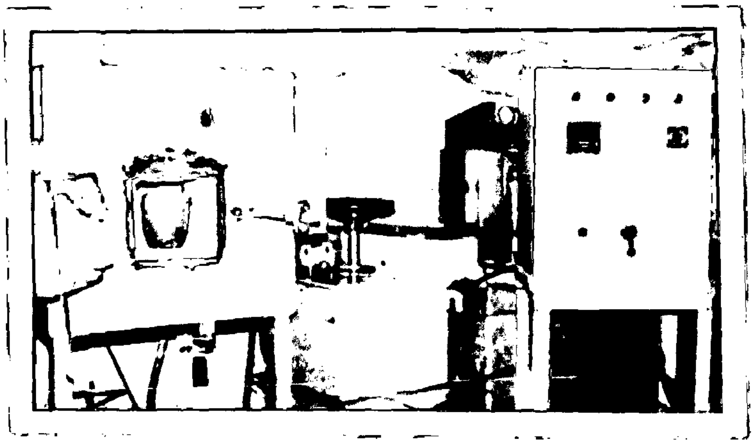


Fig. 3.1 Muffle Furnace

melting. Casting was done in a steel mould. Design of mould is shown in Fig. 3.2.

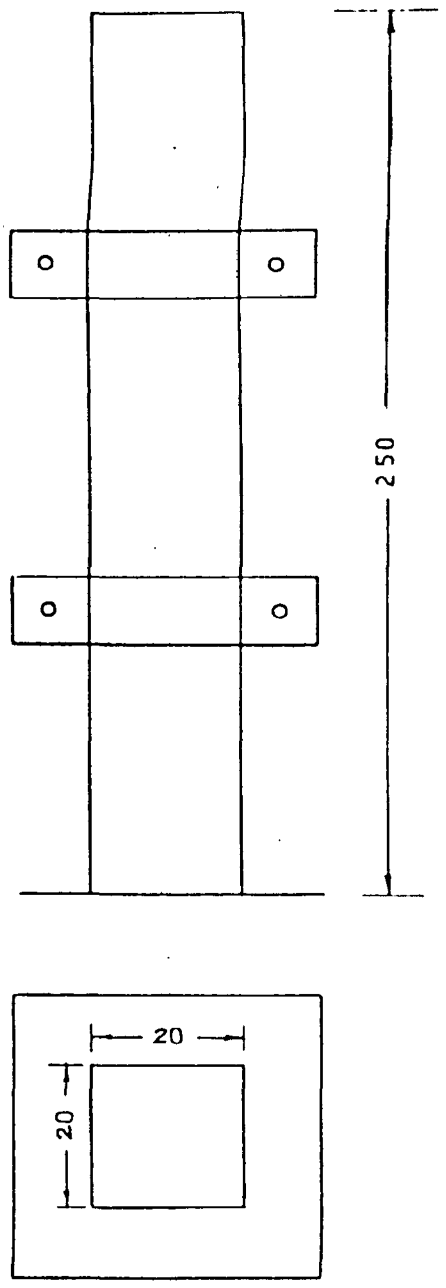
The empty crucible placed in the furnace was preheated to 900°c and the aluminium pieces were charged into the crucible. The temperature of the crucible along with aluminium pieces was raised up to 1200°c. At this temperature copper was charged into the aluminium melt and left for one hour, then zinc was added into aluminium and copper alloy melt. Degassifier (hexachloroethane) was added to the alloy melt. The melt was throughly stirred by asbestose stirrer blade. The slag that formed on the top of the melt were removed by creamic scoop. The homogenous melt was cast into the steel mould and was quenched with water. The alloy ingots were cut vertically of sizes 10x10x250 mm^3. These slices were turned into cylendrical pellets of size 5øx5 mm.

3.2 CHEMICAL ANALYSIS

By wet chemical analysis the amounts of copper and zinc in the Al-Cu-Zn alloys were determined.

3.3 LEACHING PROCEDURE

Isothermal leaching was performed on cylendrical pellets with aqueous sodium hydroxide. These experiments



ALL DIMENSIONS IN mm

FIG.3.2_ DESIGN OF THE STEEL MOULD

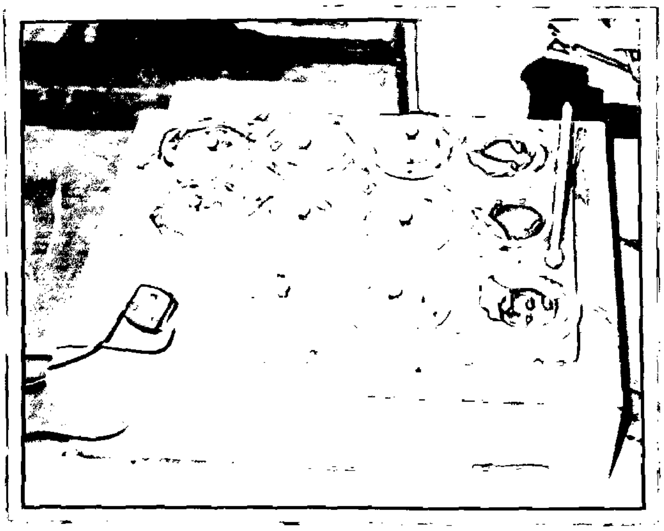


Fig. 3.3 Leaching set up

were carried out at three different temperatures 30, 40 and 50 °c and at three different concentrations of alkali (NaOH) 20, 30 and 40 wt% for a period of one hour.

Leaching was carried out by taking NaOH solutions of three different concentrations in three different 100 ml glass beakers and keeping in a constant temperature bath maintained at an accuracy of ± 0.5 °c at the required temperature, pellets were dropped in aqueous sodium hydroxide and were immersed for a period of one hour. These alloy pieces were then throughly washed with distilled water. Then they were immeresed without exposing the specimen to atmosphere in deoxygenated water in order to aviod the surface oxidation of the specimen.

3.4 SPECIMEN PREPARATION

One specimen of each casting was mounted in cold setting resin such that the top surface of the specimen was inline with the resin. These specimens were ground in grinding wheel and then polished by using emery papers from 1/0 grade to 4/0 grade. The final cloth polishing was done in blazer cloth using polishing grade alumina suspension.

The leached samples were mounted in cold setting resin such that the axis of the sample was perpendicular to that of the cold setting resin. These specimens were ground until the pellets were bisected and were polished. These specimens were coated with gold in order to form a conductive surface at the leached regions to study the surface topography under SEM and EPMA.

3.4.1 SCANNING ELECTRON MICROSCOPY

The metallographic specimens were taken under philips SEM 501 to study the morphology of the as-cast and leached alloys. The microstructures were studied at different regions. After leaching the leached thickness of the specimens were measured using μ-markers.

3.4.2 ELECTRON PROBE MICRO ANALYSIS:

The surfaces which are used in SEM were studied under JEOL Electron Probe Micro Analyser model JxA 8600 M. In this, line analysis was carried out along a line in case for the as-cast specimens and leached specimens, which gives the variation of aluminium, copper and zinc contents in these regions. Point analysis was done for as- cast alloys along different regions by taking ten different points along a line in order to ensure the concentrations of different elements. In case of leached alloys point analysis was carried out along leached regions by taking twenty different points along a line in order to ensure the concentrations of different elements.

3.4.3 X-RAY ANALYSIS:

X-ray analysis of the as-cast alloy specimens and leached specimens were carried out using philip 1140/90 X-ray diffractometer. In these analysis, copper is used as target and Nickel as the filter. The accelerating voltage of 35Kv and tube current of 20 mA was used. Scanning of the specimens were done from 5° to 90° using a chart speed of 1 cm/min.

The Bragg angle (θ) values were determined for diffraction intensity peaks. The corresponding interplanar spacings (d_{hkl}) were calculated using the following equation.

$$2d_{hkl} \, \mathrm{Sin}\theta = n\lambda$$

Where λ is the wave length of the X-ray used for study.

CHAPTER -4

RESULTS AND DISCUSSIONS

Two Al-Cu-Zn alloys were prepared and following composition was observed by wet chemical analysis.

	wt% Cu	wt% Zn	wt% Al
ALLOY- A	33.1	17.6	Rem
ALLOY- B	32.4	9.3	Rem

Scanning Electron Microscope was used to study the morphology in as-cast and in leached state. Different phases present in alloys were analysed using X-ray diffractometer and the variation in the composition of different elements were analysed by Micro Probe Analyser using line and point analysis. Subsequent section discusses the results in detail.

4.1 AS CAST ALLOY

The results of as-cast alloys under X-ray diffactometer, Scanning Electron Microscope (SEM) and Electron Probe Micro Analyser (EPMA) are as follows:

4.1.1 X-RAY ANALYSIS

Figure 4.1 shows the variation of intensity with 2θ incase of X-ray diffraction analysis for alloy B. The different intensity peaks [illegible] correspond to different Bragg angle (θ). The observed interplanar distances d_{hkl} for one of the alloys are given in Table 4.1. It is evident from the Table 4.1 that the two phases, Cu Al_2 and solid solution of Al are present in the alloy. By X-ray analysis Bridgewater et al, 1983 have identified the phases present in the Al-31.6 wt% Cu - 14.8 wt% Zn, Al-36.0 wt% Cu -13.0 wt Zn alloys as Cu(Zn) Al_2 and Al (Zn).

4.1.2 SEM STUDY

Figure 4.2 shows the SEM micrographs of as cast alloys A and B. It is evident from these micrographs that the alloys has two distinct phases. The detailed elemental analysis of these regions (White and Black) were carried out by EPMA.

4.1.3 ELECTRON PROBE MICRO ANALYSIS

Figures 4.3 and 4.4 show the lineanalysis for alloys A and B which are determined by EPMA. It is evident from the line analysis that the as cast alloys have the

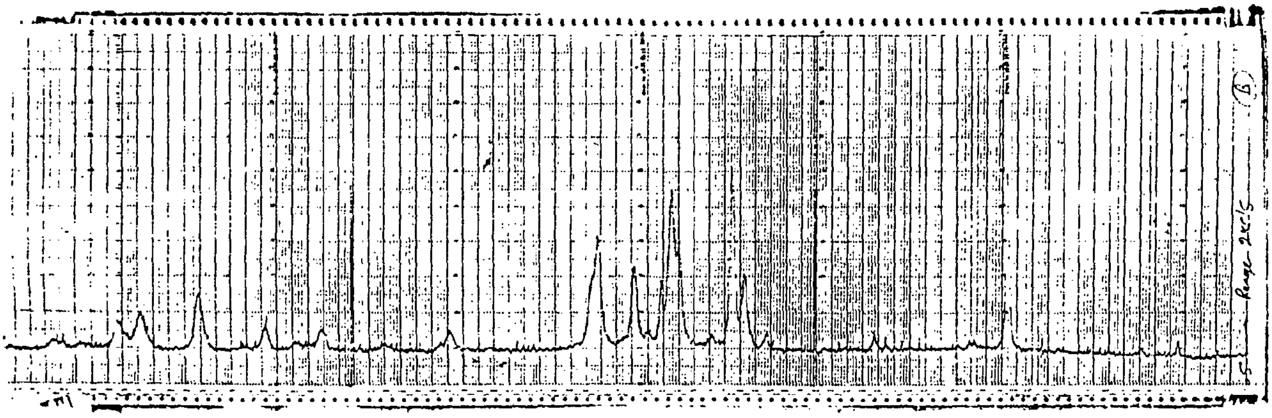


Fig. 4.1 The variation of intensity with 2θ in case of as-cast Alloy B

Table 4.1 d values of as-cast alloy B obtained by X-ray diffractometer.

	OBSERVED		PHASES IDENTIFIED			
			(Al)4F		(CuAl$_2$)12 U	
S.No	d	I/Io	d	hkl	d	hkl
1.	4.29	96			4.304	110
2.	3.048	24			3.037	200
3.	2.38	50			2.374	211
4.	2.332	100	2.338	111		
5.	2.151	65			2.146	220
6.	2.127	89			2.121	112
7.	2.023	53	2.024	200	1.919	310
8.	1.925	68			1.909	202
9.	1.621	24			1.611	222
10.	1.434	24	1.431	220	1.408	411
11.	1.366	30			1.357	420
12.	1.296	40			1.288	402
13.	1.241	32			1.234	332
14.	1.222	29	1.221	311		

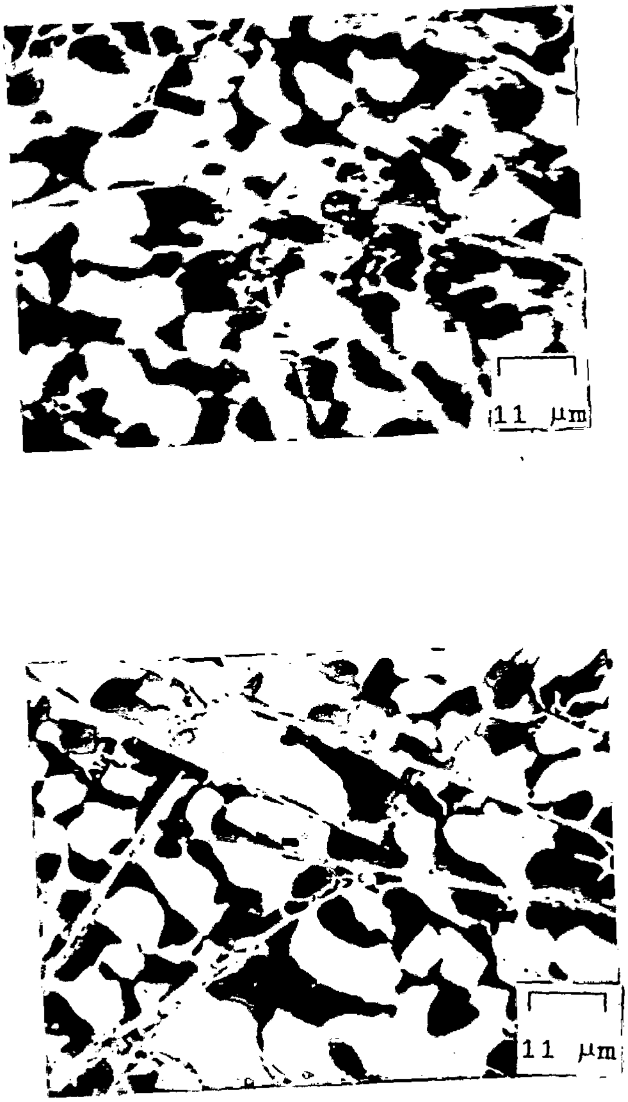


Fig. 4.2 SEM micrographs of as-cast a) Alloy A b) Alloy B

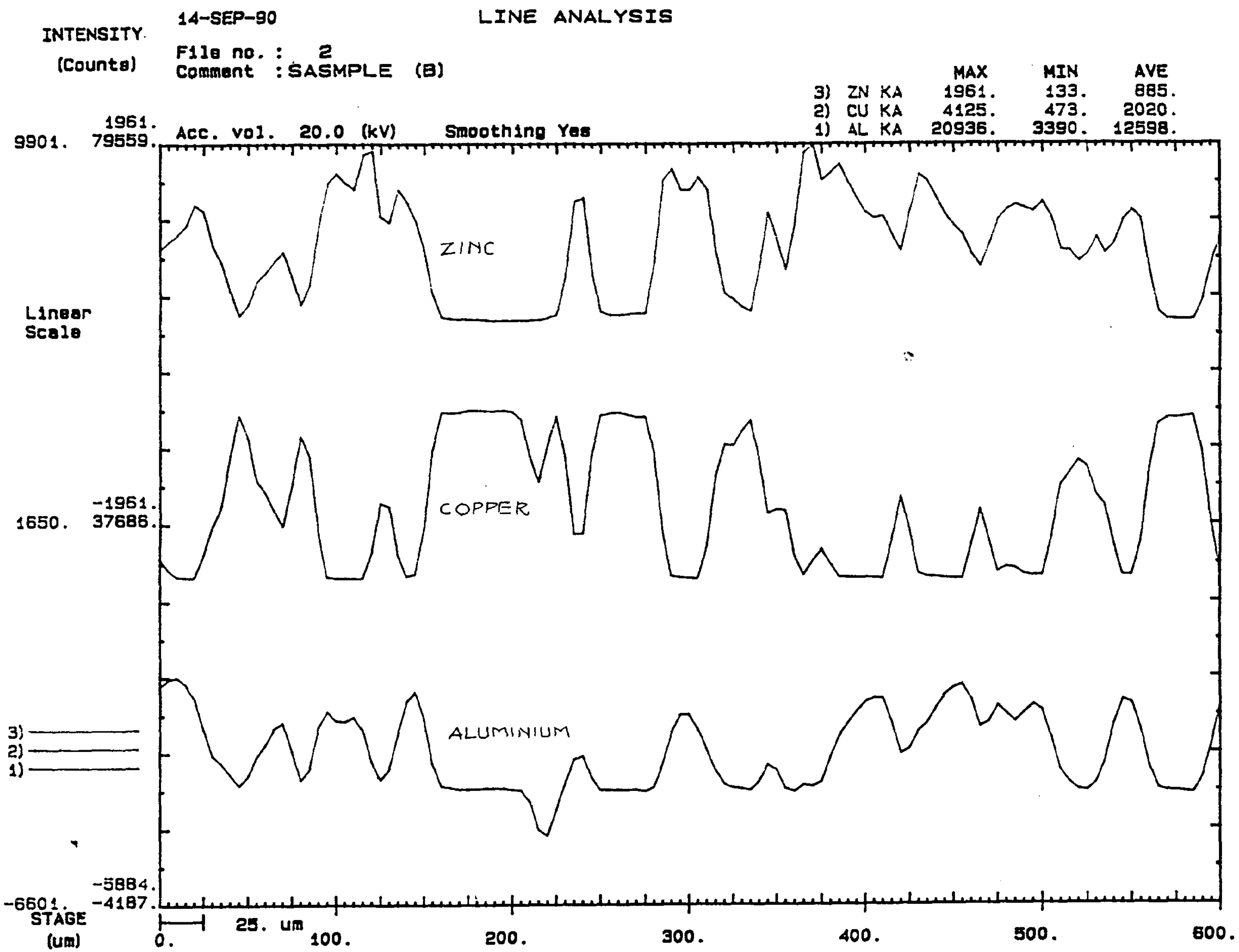
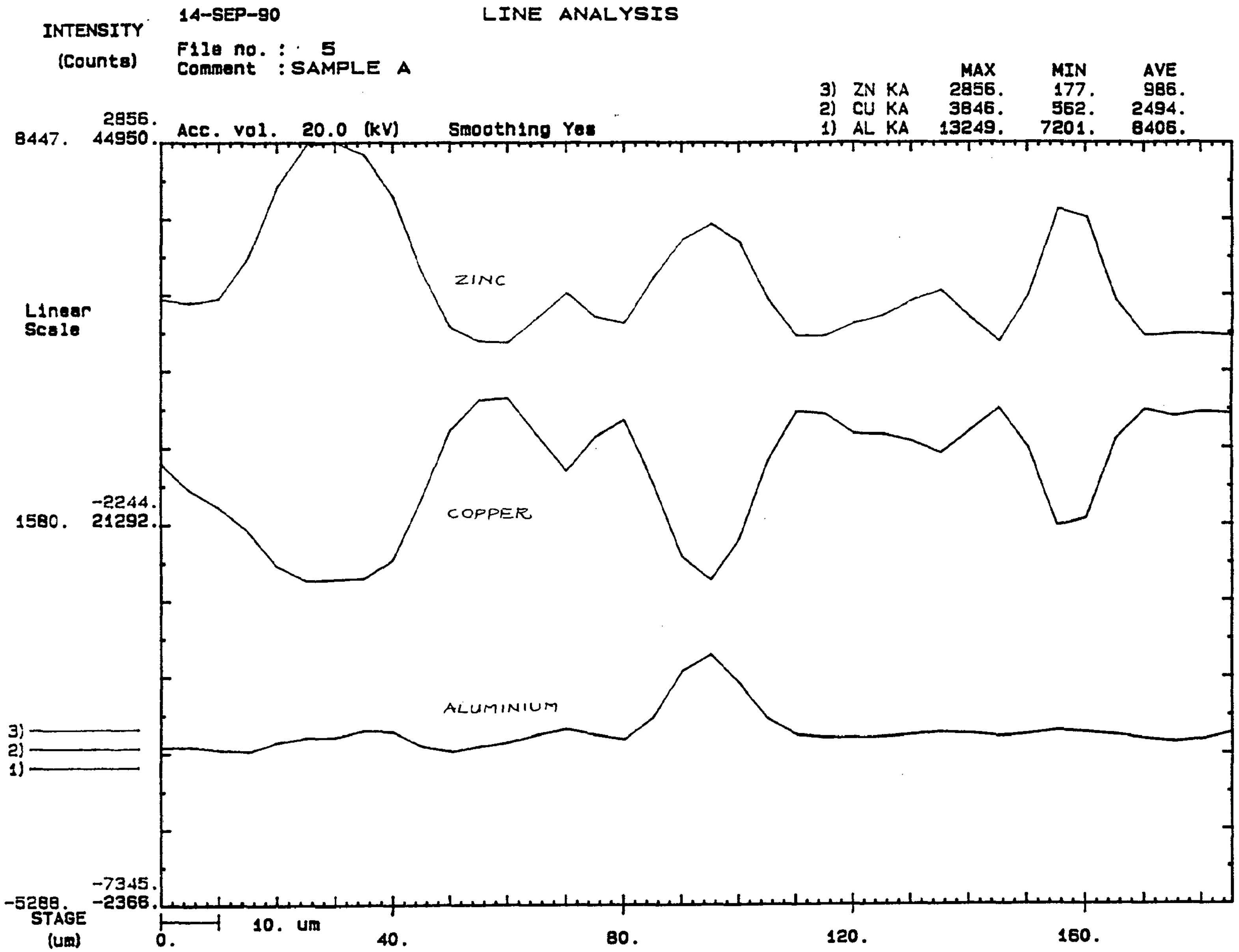


Fig. 4.3 The variation of Aluminium, Copper and Zinc in the as-cast Alloy A revealed under EPMA



	MAX	MIN	AVE
3) ZN KA	2856.	177.	986.
2) CU KA	3846.	562.	2494.
1) AL KA	13249.	7201.	8406.

Fig. 4.4 The variation of Aluminium, Copper and Zinc in the as-cast Alloy B revealed under EPMA

homogeneous variation of all three elements in the alloy matrix. There seems to have a localized fluctuation of Aluminium rich (Zinc) phase and Copper rich phase in the reverse manner. Point analysis are also carried out in different regions. It is observed that white region contains 49.9 wt% Copper and 47.0 wt% Aluminium, while the black regions contain very low amount of Copper of 4.9 wt%, higher aluminium of 67.3 wt% and 27.8 wt% of zinc. The average composition of these regions are given in Table 4.2. The variation of the concentration of aluminium, copper and zinc along different regions (White and Black) in as-cast alloys A and B are shown in Fig. 4.5 (a) and (b) and 4.6(a) and (b). It is seen that the variation of amounts of all three elements along black region shows the coreing effect. Friedrich et al, 1981 showed that no concentration gradient existed in any of the phases with in the alloys and at the interface a discontinuous change in concentration for all three metals was observed. But the aluminium solid solution contains solutes of zinc and copper, when this phase solidifies coreing effect is probable to occur as observed in our investigation.

4.2 LEACHED ALLOY:

The results of leached alloys under SEM, EPMA and X-ray analyser are as follows:

Table 4.2 Average elemental concentration of Aluminium, Copper and Zinc along Black and White regions of as-cast alloy A

% wt of metal	Region	
	Black	White
Aluminium	67.3	47.0
Copper	4.9	49.9
Zinc	27.8	3.1

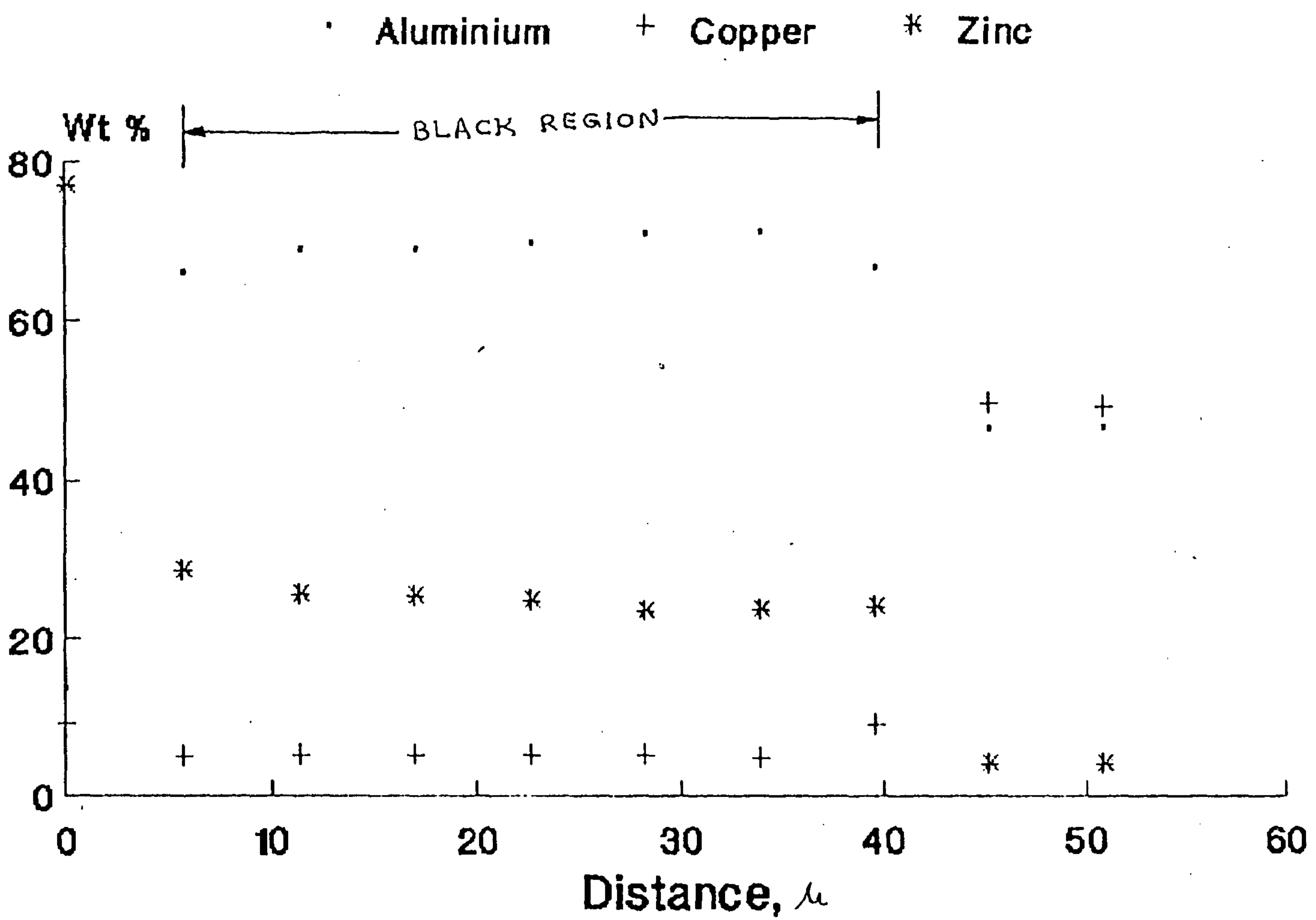


Fig.4.5(a) The variation of Aluminium, Copper and Zinc in Alloy A along Black region

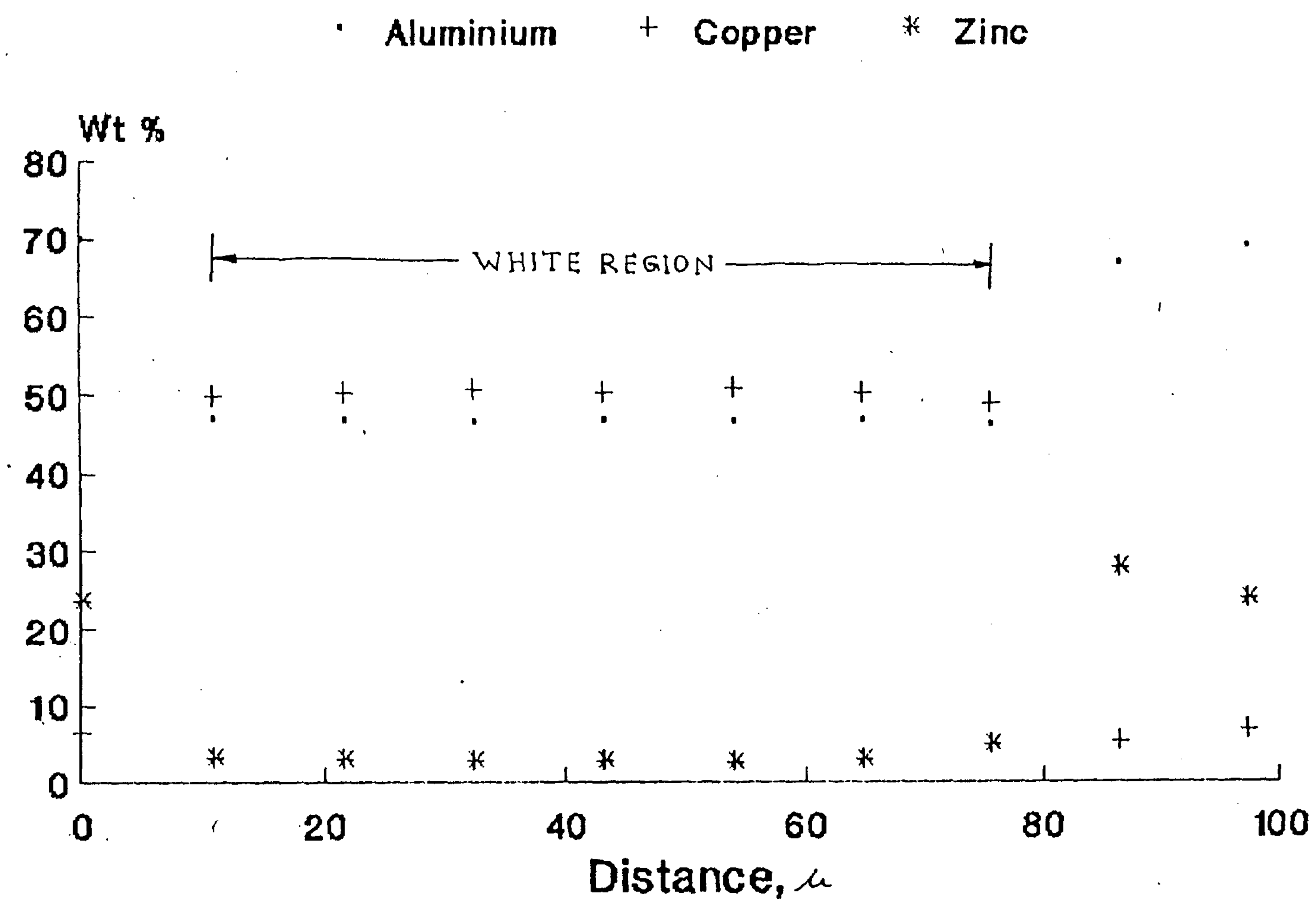


Fig. 4.5(b) The variation of Aluminium, Copper and Zinc in Alloy A along White region

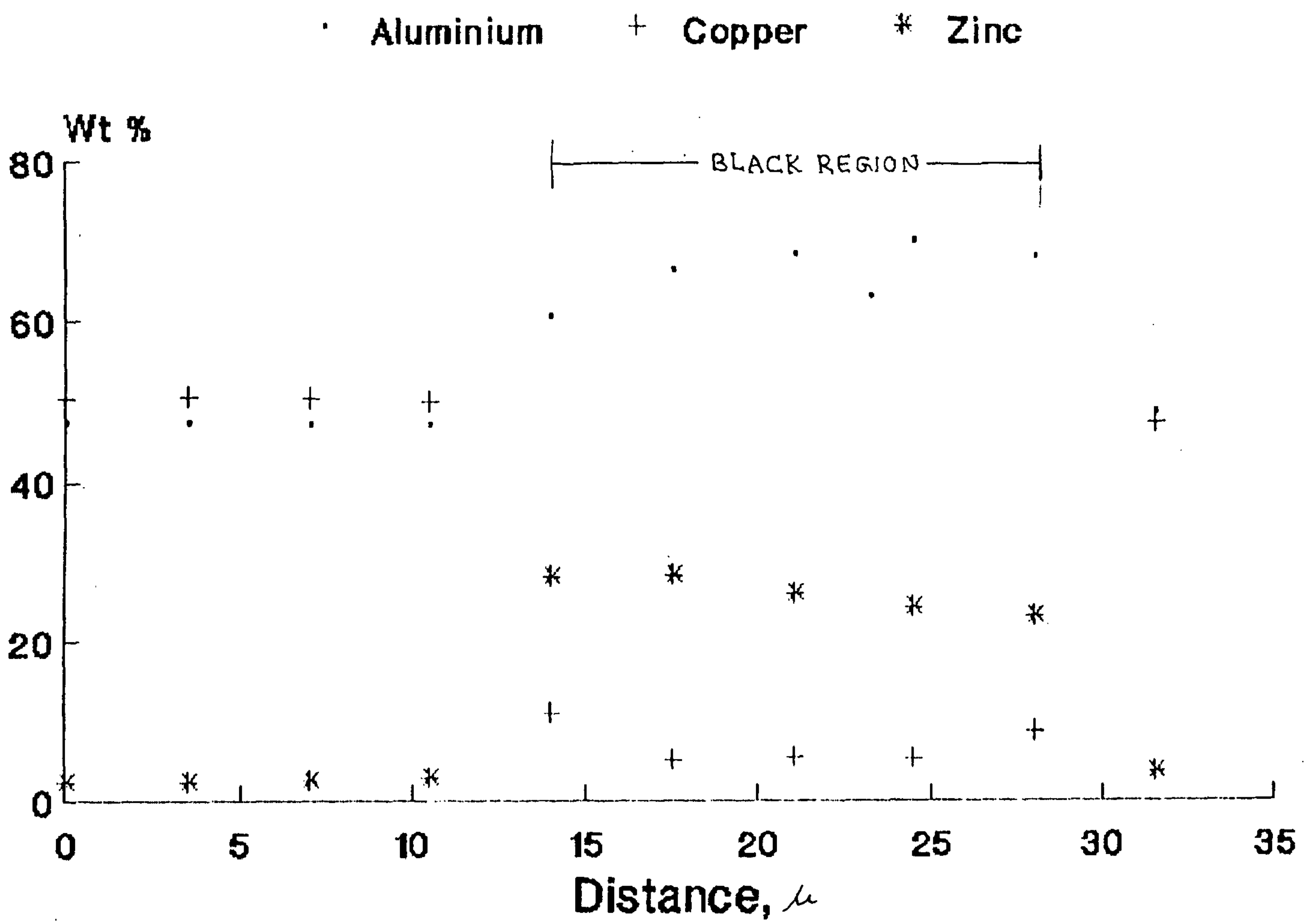


Fig.4.6(a) The variation of Aluminium, Copper and Zinc in Alloy B along Black region

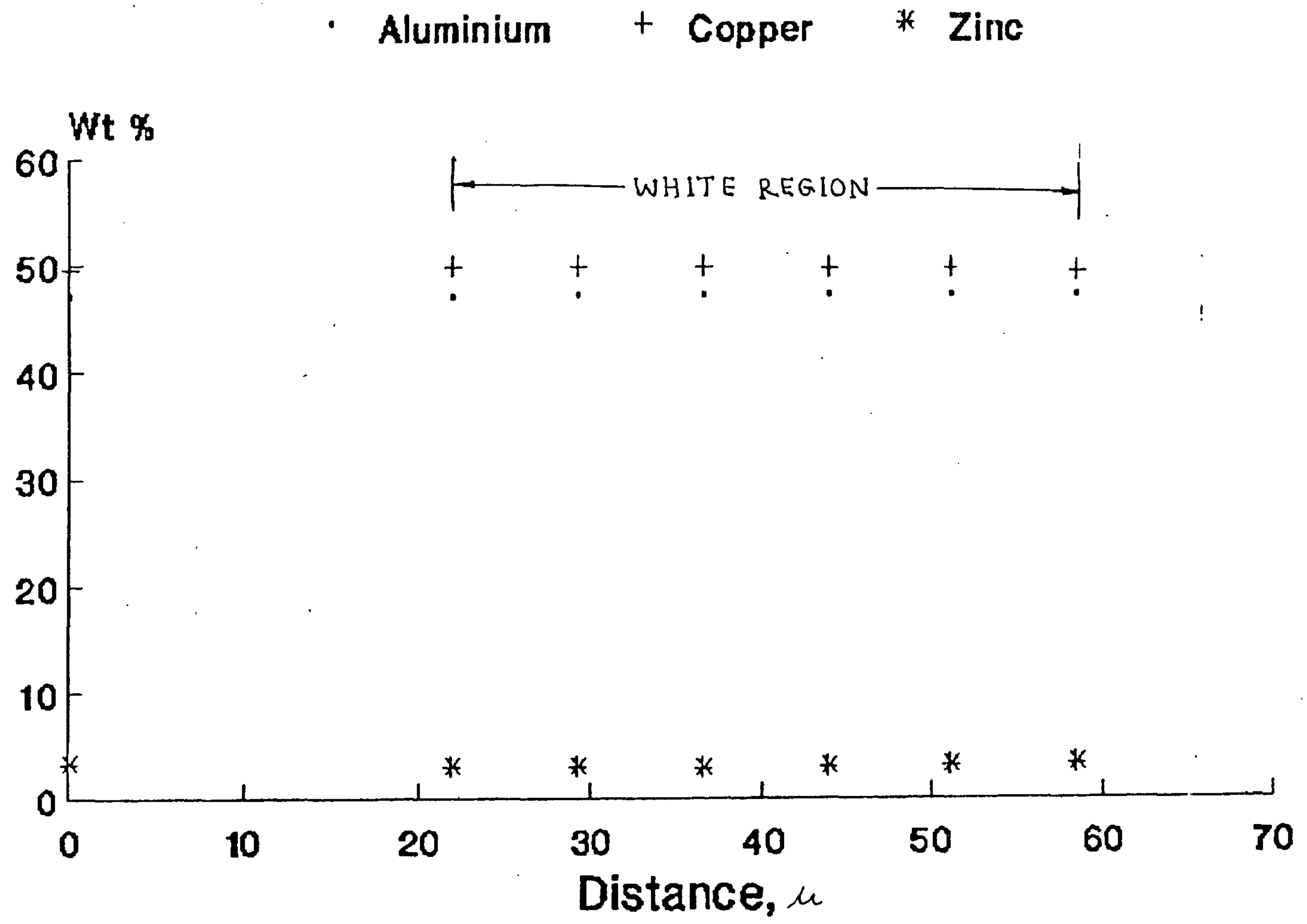


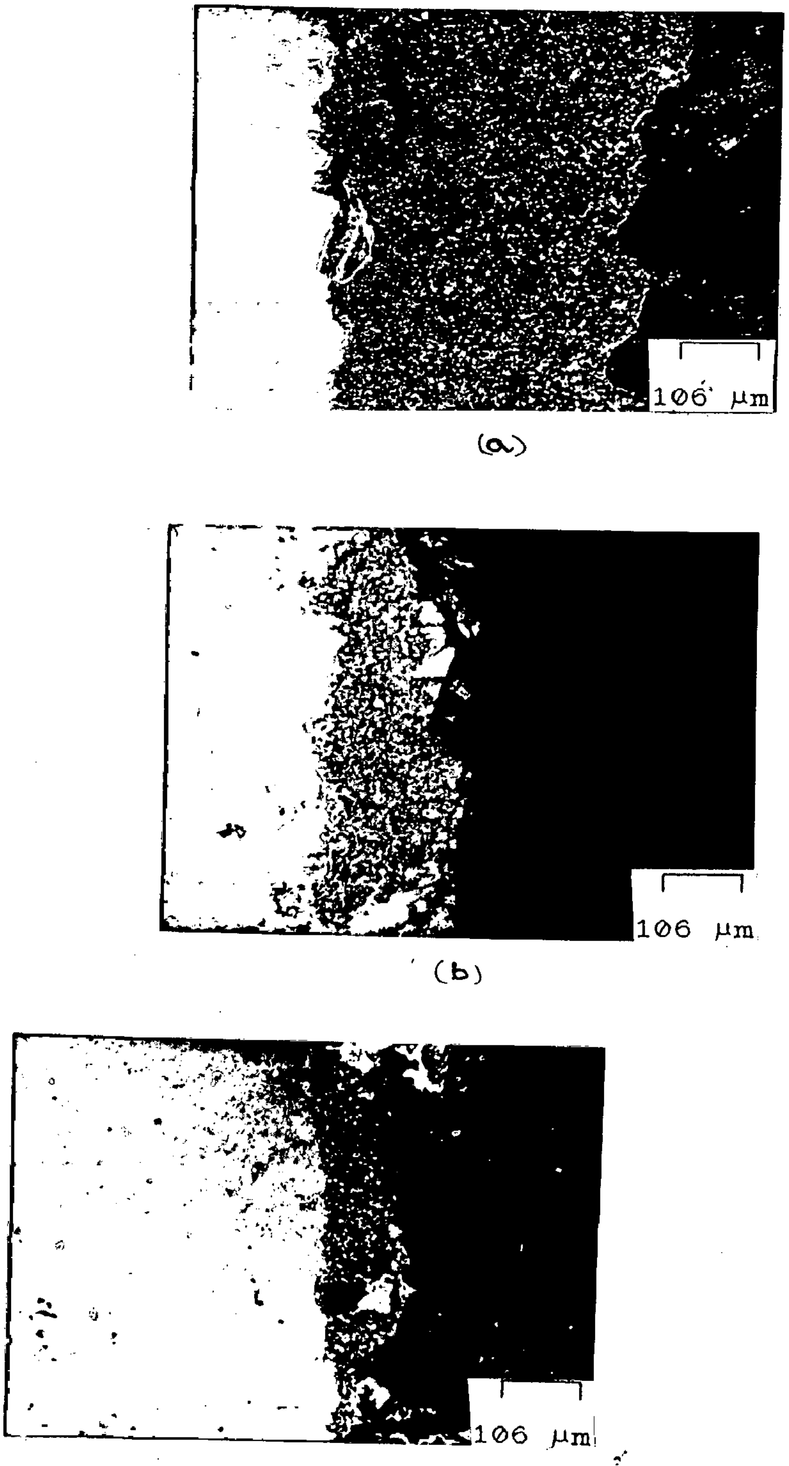
Fig.4.6(b) The variation of Aluminium, Copper and Zinc in Alloy B along White region

4.2.1 SCANNING ELECTRON MICROSCOPY

The SEM micrographs, Fig. 4.7 and Fig. 4.8 show the vertical section of the pellets in the leached surface layer and uneffected alloy matrix for both the alloys. In all reaction conditions investigated, for all samples a defined boundary is observed to exist and is parallel to the original alloy surface. For both the alloys the boundary propogates from the surface with increase in leaching temperature. Figure 4.9(a) and (b) show the variation of leached thickness with temperature.

For both alloys, the leached thickness also increased with increase in the NaOH conc. (Fig. 4.10 and Fig 4.11). Figures 4.12(a) and (b) show that the variation of leached thickness with varying concentrations of NaOH . It is evident from Fig 4.7 to 4.12 that the leaching rate increases with temperature and concentration of NaOH. Curry-Hyde et al 1987, Tomsett et al 1984 have also observed similiar nature of increase in leached thickness with temperature and concentration of NaOH.

It is evident from Fig. 4.13 (a) that the black region containing solid solution of Aluminium is leached out while the white region seems to be comparatively stable. This occurs due to the electrode potential difference developed



(a)

(b)

(c)

Fig. 4.7 The variation of leached thickness with different Temperature °c, when leached with 20 wt% Sodium hydroxide for 1 h. for Alloy A a) 50°c b) 40°c and c) 30°c

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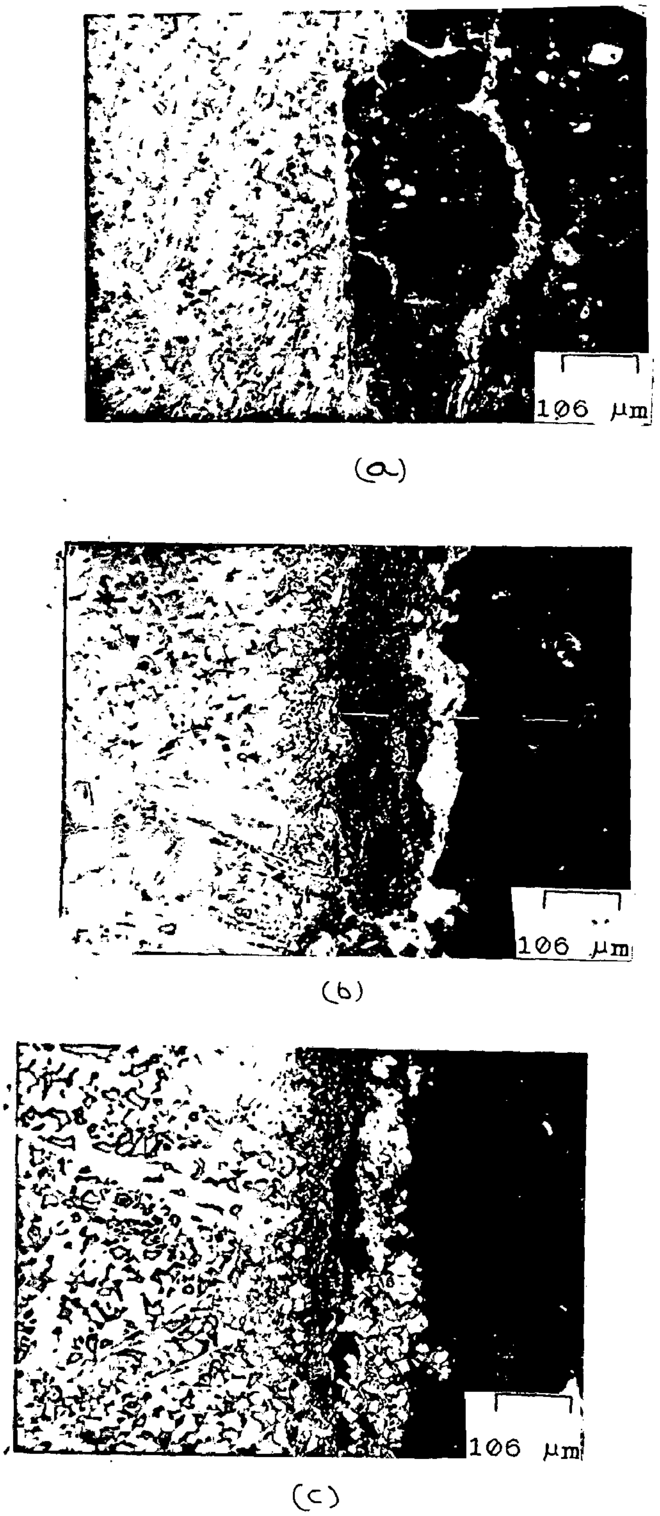


Fig. 4.8 The variation of leached thickness with different Temperature °c, when leached with 20 wt% Sodium hydroxide solution for 1 h. for Alloy B, a) 50°c b) 40°c and c) 30°c

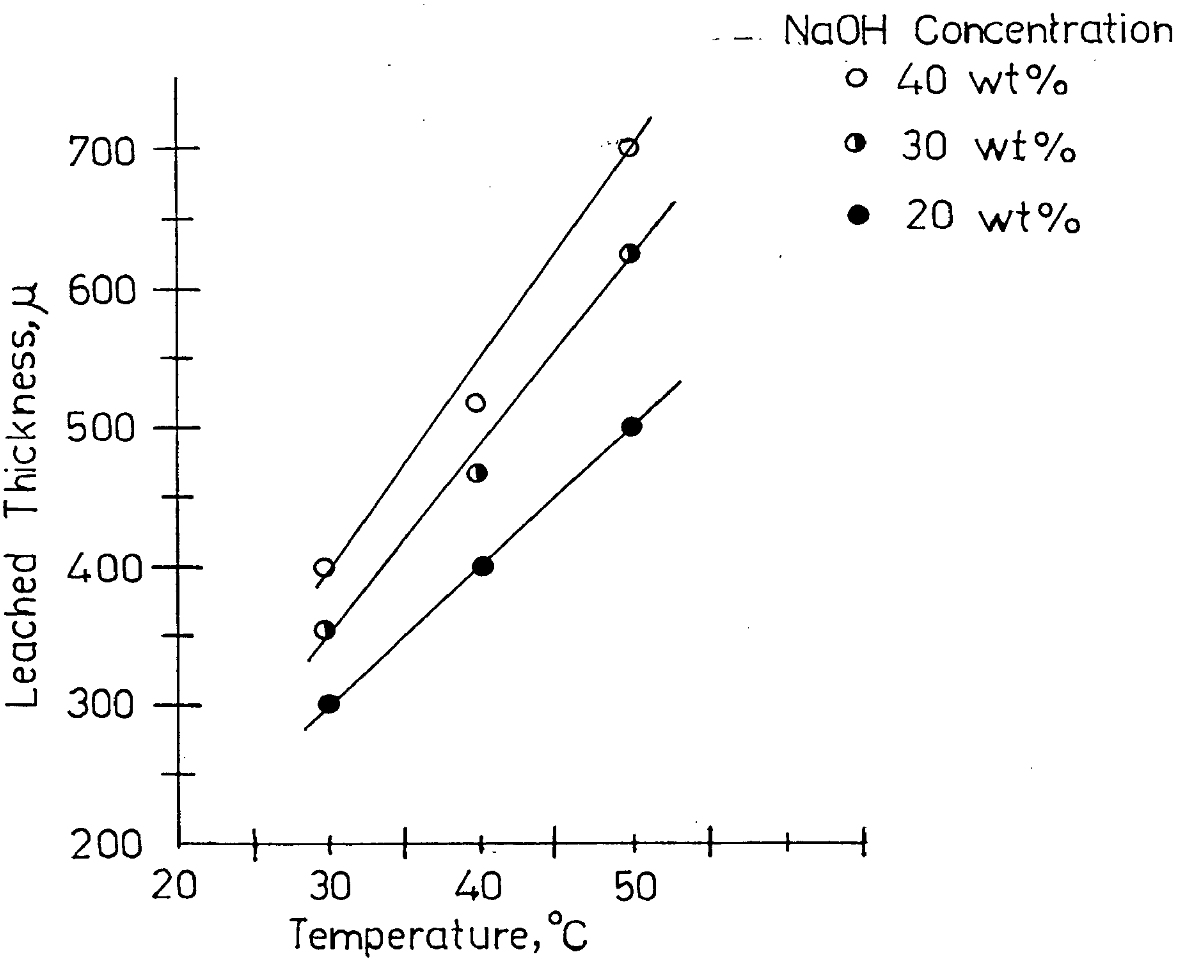


Fig. 4.9(a) The variation of leached thickness with Temperature °c for Alloy A

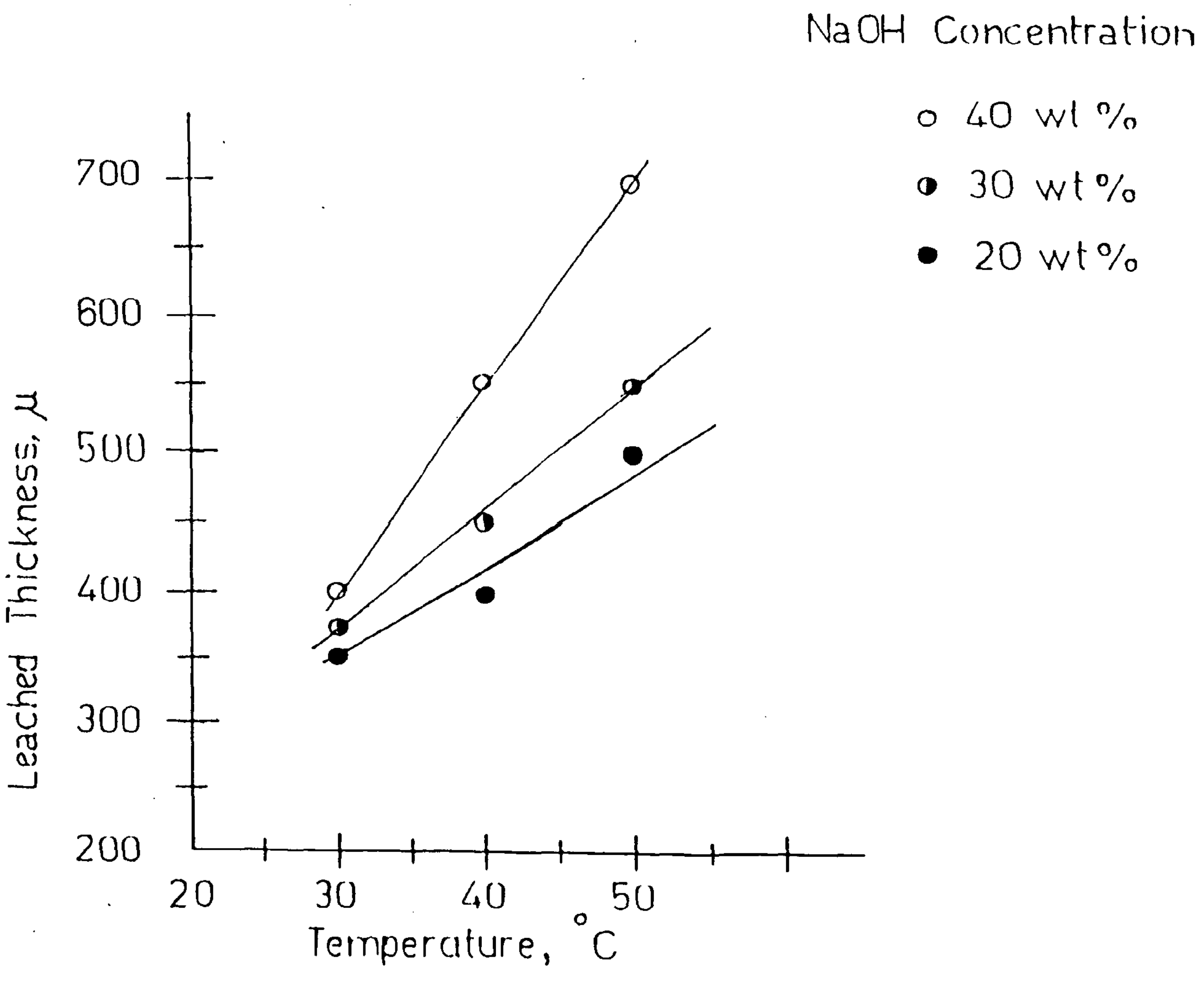


Fig.4.9(b) The variation of leached thickness with Temperature °C for alloy B

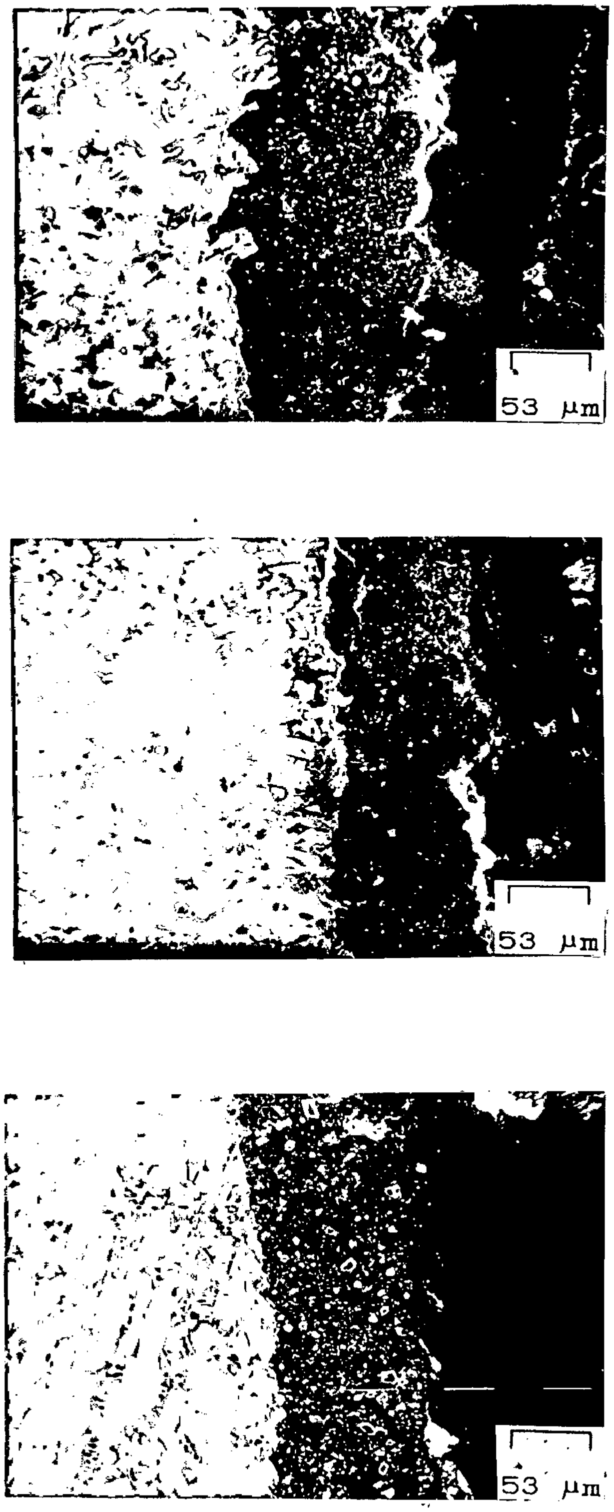


Fig. 4.10 The variation of leached thickness with Sodium hydroxide concentration, when leached at 30°c for 1h. for Alloy A, a) 40 wt% b) 30 wt% and c) 20 wt%

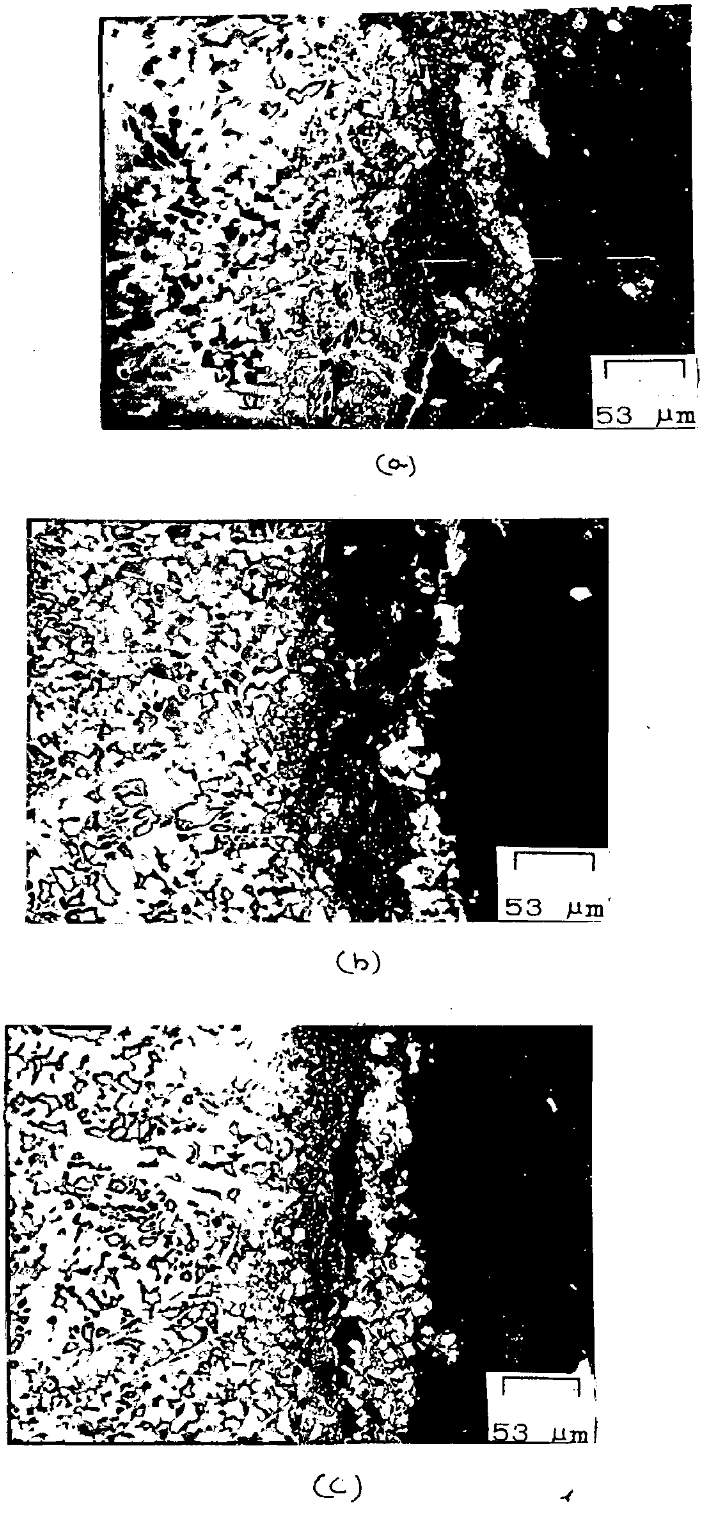
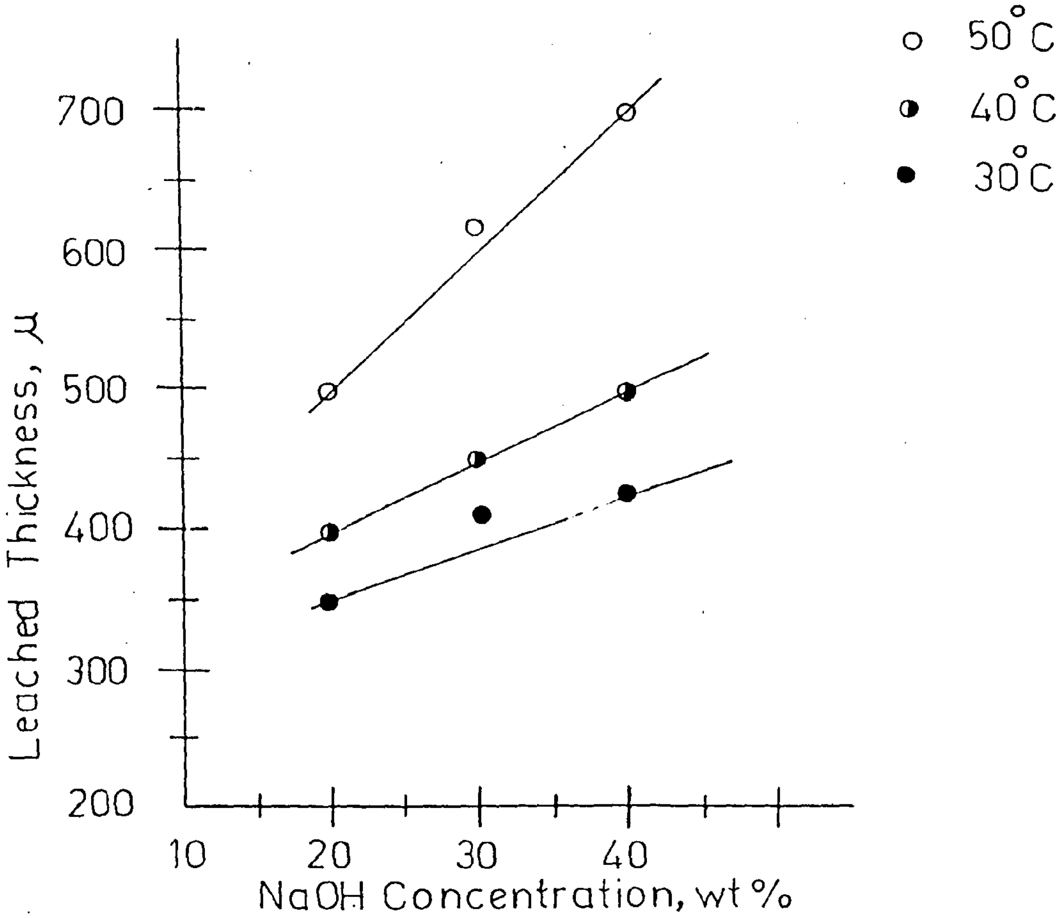


Fig. 4.11 The variation of leached thickness with Sodium hydroxide concentration, when leached at 30°c for 1h. for Alloy B, a) 40 wt% b) 30 wt% and c) 20 wt%



ig. 4.12(a) The variation of leached thickness with Sodium hydroxide concentration for Alloy A

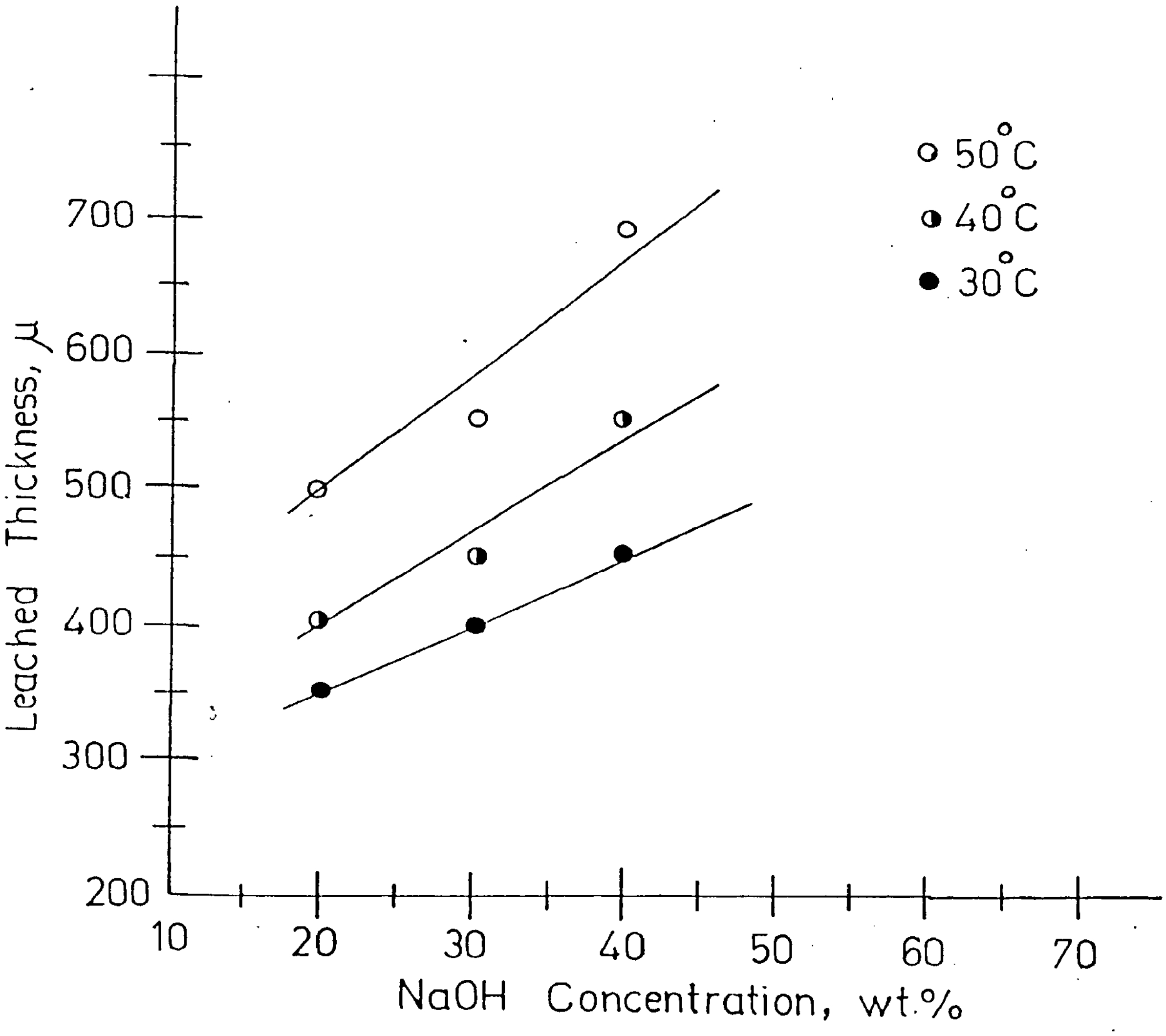


Fig.4.12(b) The variation of leached thickness with Sodium hydroxide concentration for Alloy B

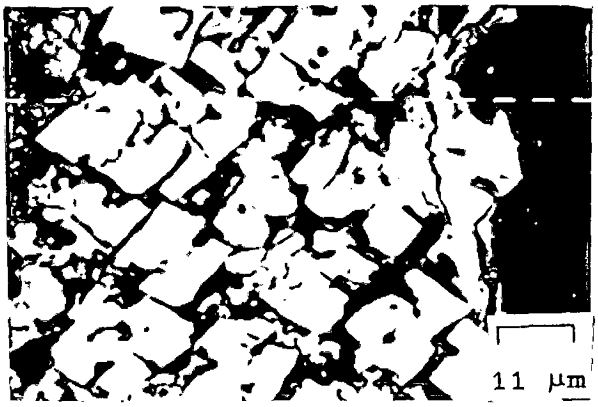


Fig.4.13(a) SEM micrograph of section through partially leached alloy A, at 30°c with 20 wt% Sodium hydroxide solution for 1h., showing preferential dissolution of anodic region (Solid solution of Al)

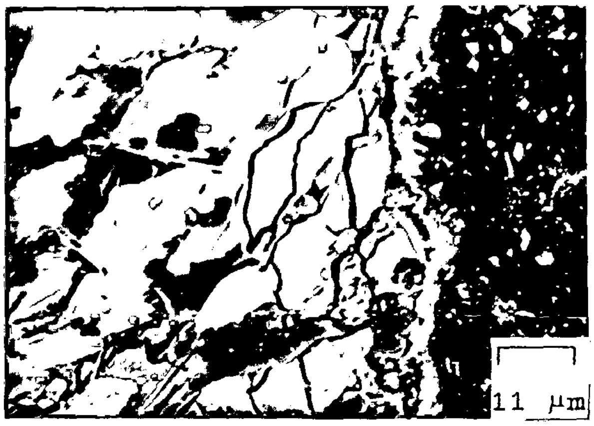


Fig.4.13(b) SEM micrograph of section through partially at 40°c with 40 wt% NaOH solution leached alloy A, showing cracks nucleated and propagated at the interfacial region between solid solution of Aluminium and $CuAl_2$ phase

between the two phases. These two phases are electrically short circuited through the body of the alloy. As soon as the alloy is in contact with the aqueous sodium hydroxide solution local cell action takes place and dissolution takes place at anode . In this case the anode is the solid solution of Aluminium (Metal HandBook, Corrosion, V-9, 1987, Uhlig, 1963).

Fig 4.13(b) shows the SEM micrograph of the alloy A, leached at 40°c with 40 wt% NaOH for one hour. It is seen that cracks are nucleated and propagated at the interfacial region between the aluminium solid solution and $CuAl_2$ phases due to the residual of stresses developed at these regions and contact with the aqueous sodium hydroxide.

4.2.2 ELECTRON PROBE MICRO ANALYSIS:

Figures 4.14(a). to (c) show the line analysis by Electron Probe for the leached samples of alloy A. It is evident from figure 4.14 (a) to (c) that the Zinc and Aluminium concentration decreased uniformaly in the leached portion. Where as the amount of copper is proportionally higher in the leached region. In order to find out the variation in amount of elements (Aluminium, Copper and Zinc) point analysis is carried out at the leached regions. Figure 4.15 shows the point analysis results across the leached and

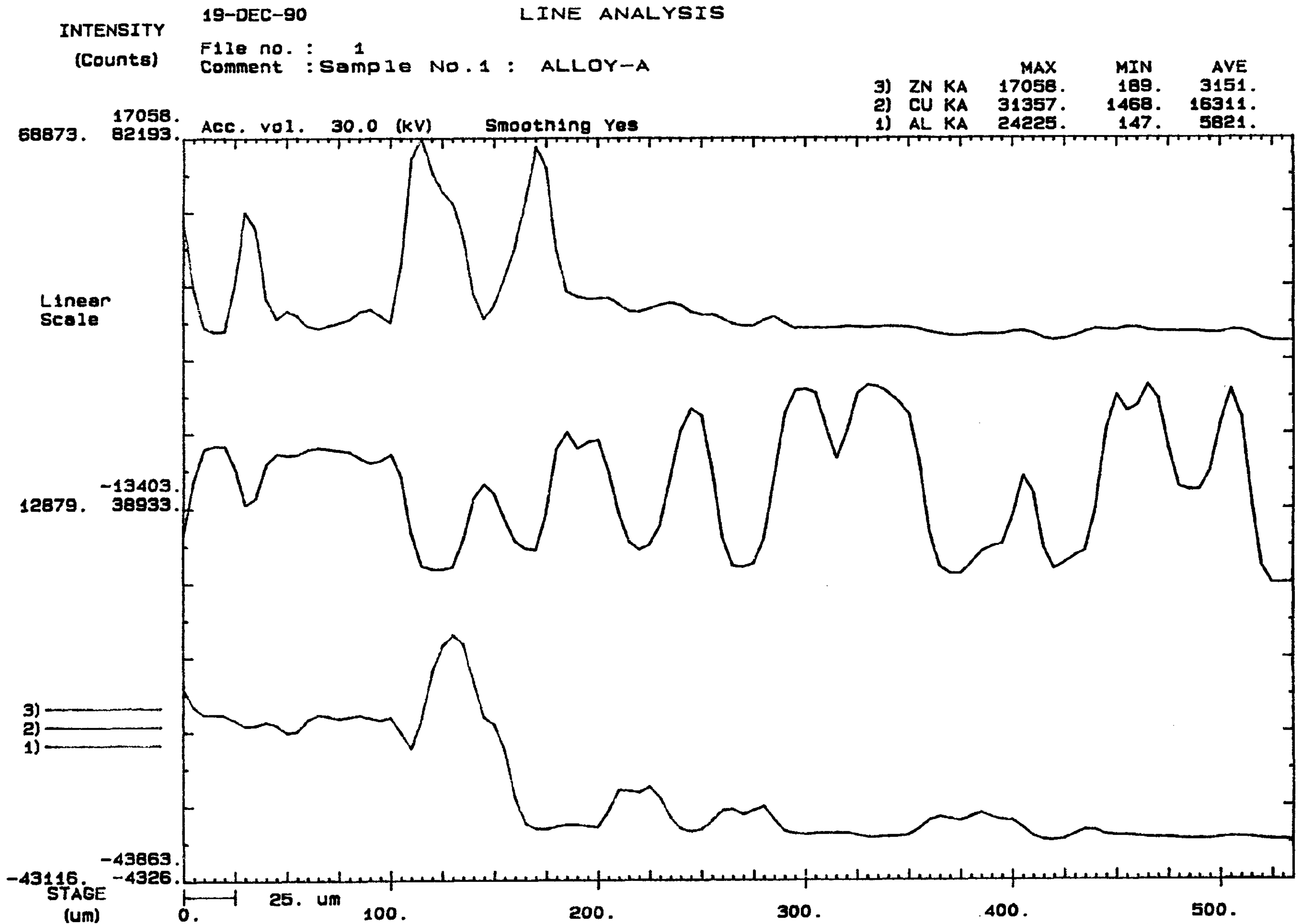


FIGURE 4.14(a) THE VARIATION OF ALUMINIUM, COPPER AND ZINC IN THE ALLOY A, LEACHED AT 50°C AND 20 wt%

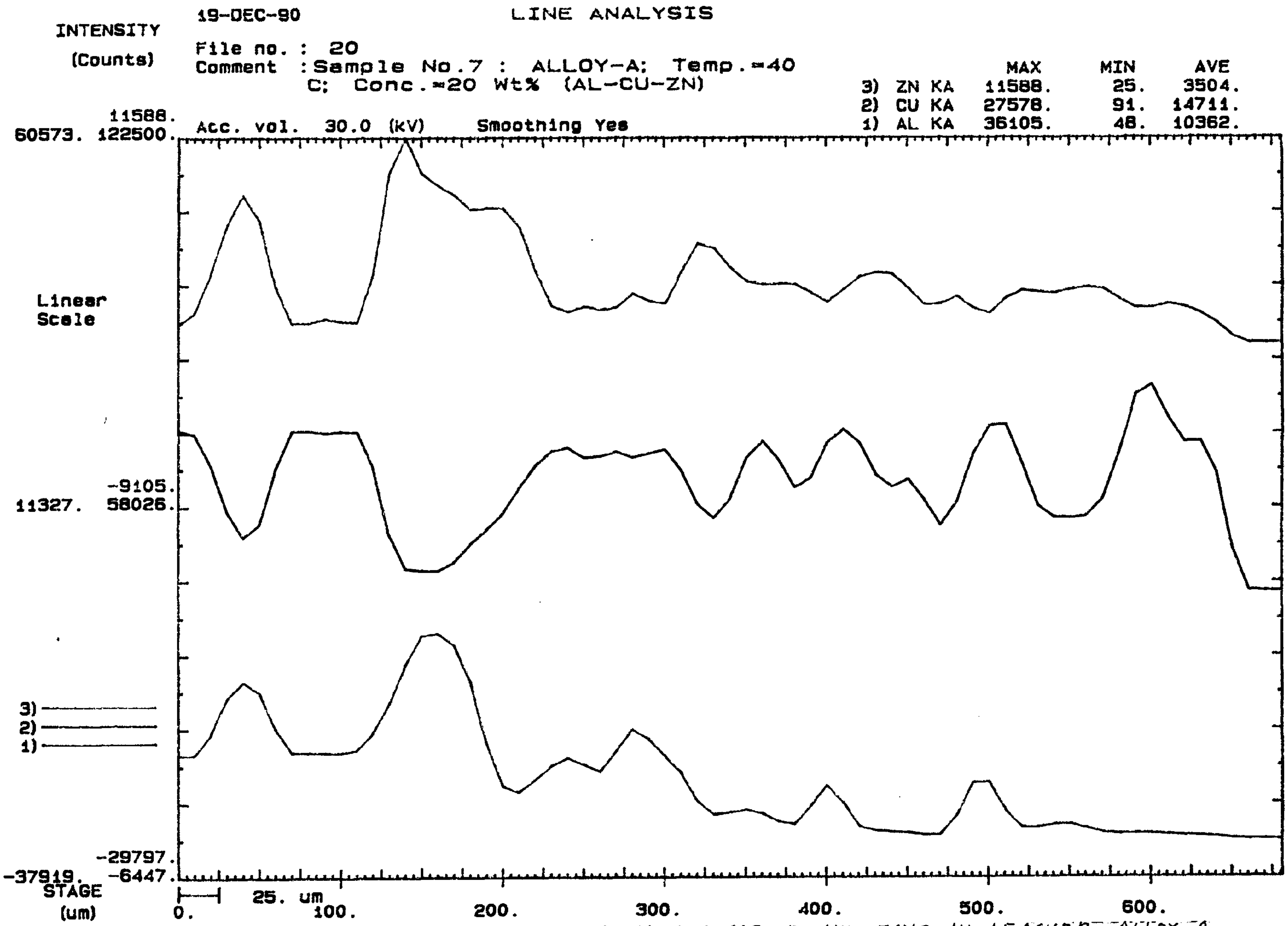


FIGURE 4.14(b) THE VARIATION OF ALUMINIUM, COPPER AND ZINC IN LEACHED ALLOY A

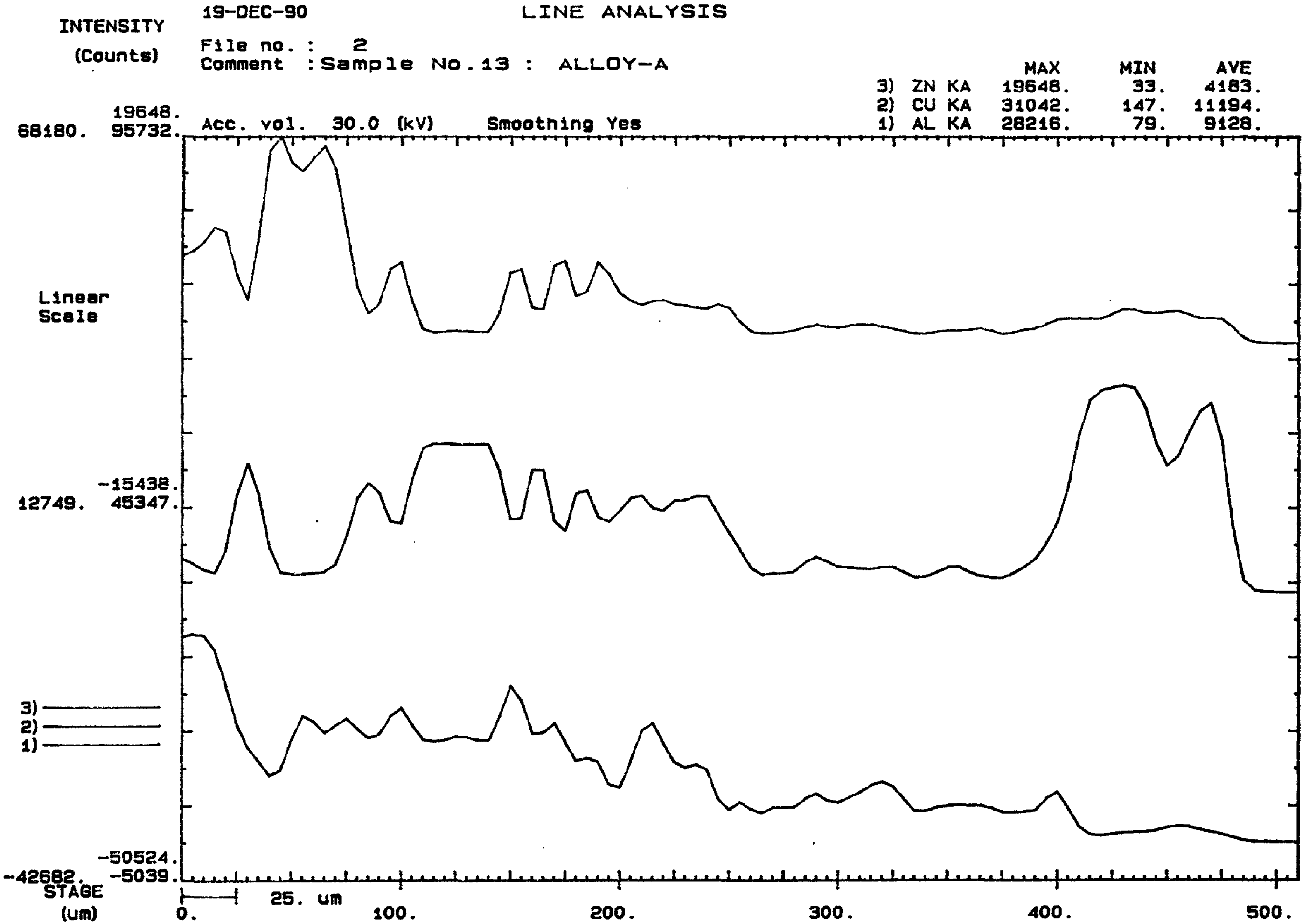


FIGURE 4·14 (c) THE VARIATION OF ALUMINIUM, COPPER & ZINC IN LEACHED ALLOY A

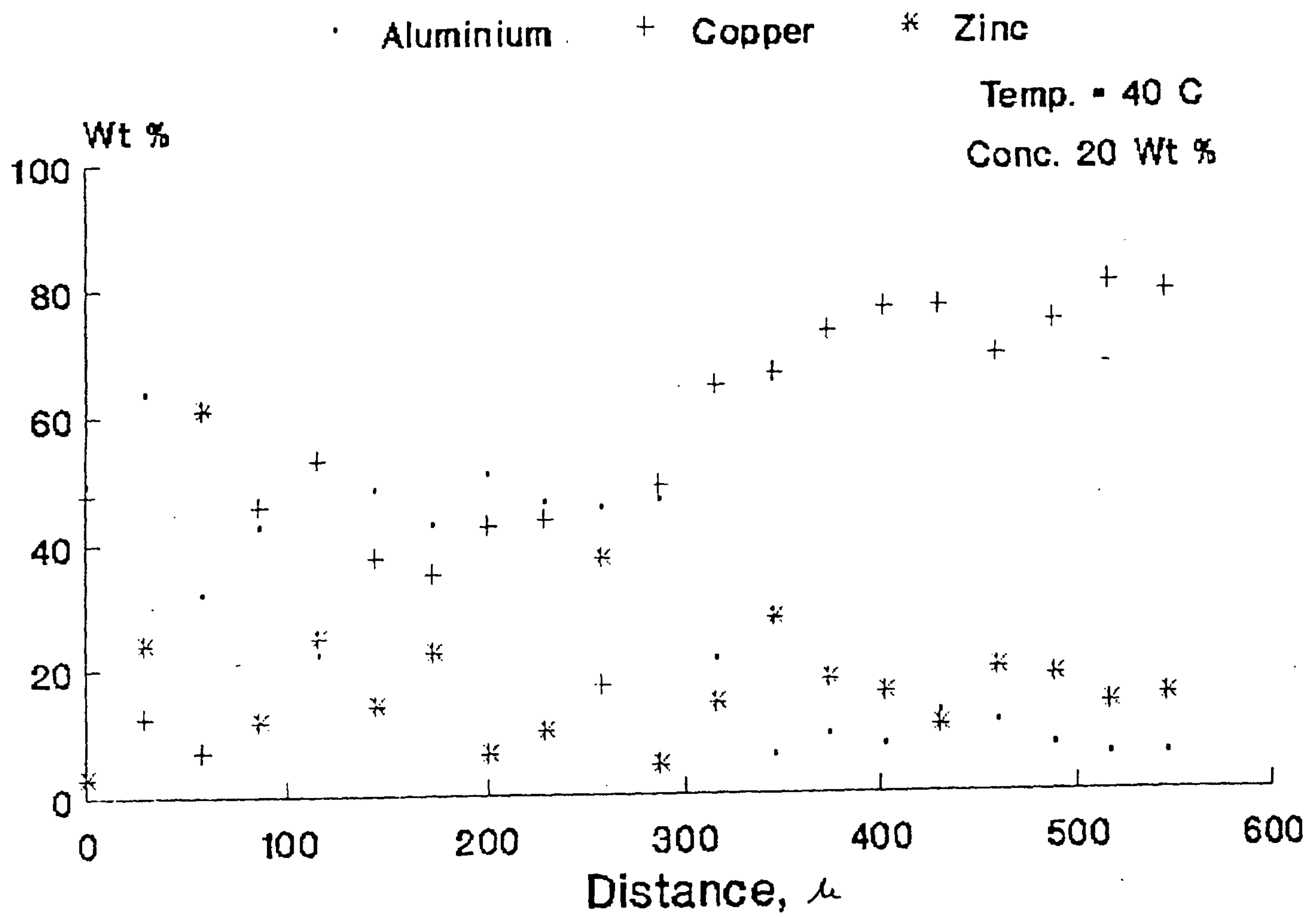


Fig. 4.15 The variation of Aluminium, Copper and Zinc in alloy A along leached and unleached regions

unleached region. The concentration of various elements in the leached product zone were less than 100%. This could be due to the formation of oxide nature of the sample (Friedrich et al 1981).

Figure 4.16 shows SEM micrograph of alloy A leached at 30°c with 40 wt% NaOH .The black areas in the leached region, show the porous regions which is confirmed by point analysis under EPMA. In the white areas the amount of the relative Copper concentration is high, which is due to the leaching of Aluminium from $CuAl_2$ phase shown by the following equation(Thomsett et al 1984).

$$Cu\,Al_2(S) + 2OH^- + 6H_2O \text{-----}{>} Cu(S) + 2Al(OH)^-_4\ (aq) + 3H_2(g)$$

4.2.3 X-RAY ANALYSIS

Figure 4.17 shows the variation of intensity with 2θ in case of X-ray diffraction analysis for fully leached alloy B. The different intensity peaks corresponds to different Bragg angle (θ). The observed interplanar distances d_{hkl} for one of the fully leached alloys are given in Table 4.3. It is evident from the Table 4.3 that the two phases (Copper and Cu_2O) are present in the fully leached alloys. Similar effect has been observed by Bridge water et al 1983. Micro Probe analysis showed that the leached alloy also conatined 7 wt% Aluminium and 3 wt% Zinc. However from X-Ray analysis, we could not get any peaks corresponding to Al and Zn.

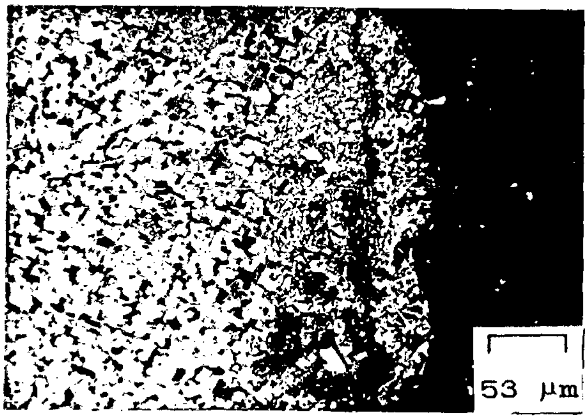


Fig. 4.16 SEM micrograph of section through partially leached alloy A at 30°c with 40 wt% Sodium hydroxide solution, showing porous region at leached portion

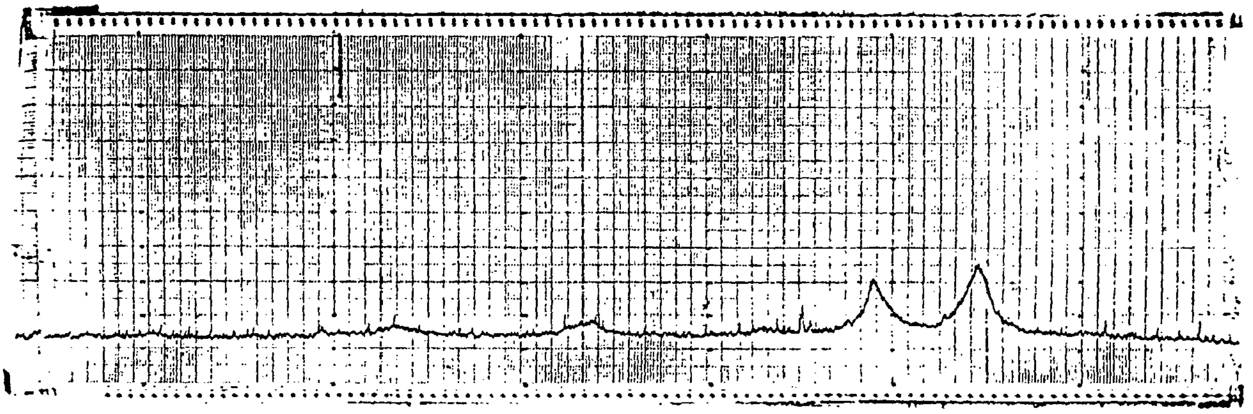


Fig. 4.17 The variation of intensity with 2θ in case of fully leached alloy B

Table 4.3 d values of fully leached alloy B obtained by X-ray diffractometer.

	OBSERVED		PHASE IDENTIFIED			
			(Cu)4F		Cu_2O 6c	
S.No	d	I/Io	d	hkl	d	hkl
1.	2.459	100			2.465	111
2.	2.092	88	2.088	111	2.135	200
3.	1.901	68	1.808	200	1.743	211
4.	1.499	51			1.510	220
5.	1.276	54	1.278	220	1.287	311

CHAPTER— 5

CONCLUSIONS:

1. Micro Probe results and X-ray diffraction results showed that the two phases $CuAl_2$ and solid solution of Aluminium are present in the as-cast Al-33.6 wt% Cu-17.6 wt% Zn and Al-32.4 wt% Cu-9.2 wt% Zn alloys.

2. Coring effect has been observed in the solid solution of Aluminium containing Copper and Zinc.

3. For both alloys, the leached thickness increased with increase in temperature and sodium hydroxide concentration.

4. While leaching, solid solution of Aluminium is leached out. This is due to the electrode potential difference developed between the two phases. These two phases are electrically short circuited through the body of the alloy. As soon as the alloy is in contact with the aqueous sodium hydroxide solution, local cell action takes place and dissolution takes place at anode.

5. It is observed from the Electron Probe Microscopic Analysis, that the concentration of Aluminium and Zinc decreased unifromely in the leached region, where as the amount of Copper is proportionally high.

6. It is observed that the Aluminium is leached out from $CuAl_2$ phase.

7. X-ray diffraction results showed that the two phases Cu and Cu_2O are present in the fully leached alloys.

SUGGESTION FOR FUTURE WORK

1. It is suggested that the solutes like Vanadium, Magnesium, Maganese, Palladium, Rhodium and Cromium should be added to the Al-Cu-Zn alloy and the effect of these additions on the leaching characteristics should be studied along with their activities.

2. The leaching characteristics of 50 wt% Al-30-36 wt% Cu-14-20 wt% Zn alloy should be studied at low temperatures and high concentrations of NaOH, by varying leaching time.

3. The central hole may be prepared cylindrical pellets to increase the surface area and reduces the pressure drop in the catalytic bed. The spherical pellets and spherical pellets with a central hole can also be tried.

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