AN ANALYSIS OF SECOND PHASE PARTICLES

IN ZIRCALOY 2

by

PIERRE LEON JACQUES CHEMELLE

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ABSTRACT

The different second phase particles present in zircaloy 2 in the annealed and in the cold worked, stress relieved conditions were analyzed by transmission electron microscopy (TEM) and by scanning transmission electron microscopy (STEM) of thin foils. The crystallographic structure of each phase was determined by selected area electron diffraction with the TEM and the chemical composition was obtained by energy dispersive X-Ray microanalysis with the STEM.

In zircaloy 2, two intermetallic phases are present as particles of 0.1 to 1 μm diameter uniformly distributed within an α zirconium matrix which contains tin in solid solution. One of the intermetallic phases has a hexagonal structure similar to $ZrCr_2$ ($a_0 = 5.1$ Å, $c_0 = 8.3$ Å) and a composition close to $ZrCr_{1.1}Fe_{0.9}$. This phase is often present as angular particles with twins or stacking faults on (0001) planes. The second intermetallic phase is a nickel-iron-zirconium compound of composition $Zr_2Ni_{0.4}Fe_{0.6}$ with the tetragonal structure of Zr_2Ni (a_0=6.5 Å c_0=5.3Å). In annealed zircaloy 2 individual particles were observed as well as heterogeneous clusters of particles. In addition to these phases, inclusions of 1 μm were identified as Zr_3Si. Scanning electron microscopy of chemically polished surfaces showed only the chromium rich phase as the nickel rich phase was dissolved by the chemical etching.

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I. INTRODUCTION

I.1. Historical background

Even though zirconium is more abundant in the earth's crust (0.03%) than lead, copper, nickel or zinc, it has been known only for the last two centuries. Discovered in 1789 by the German chemist Klaproth in a "jargon" of Ceylon, the element zirconium was not isolated in its metallic form until 1824 when Berzelius obtained an impure metal powder by reducing potassium fluorozirconate with metallic potassium. Hafnium, which is always associated with zirconium in the ore (about 2%), was not isolated until 1923 (Costes and Hevesy). In 1925 Van Arkel, Deboer and Fast prepared the pure metal by decomposition of the iodide. In 1944 W. J. Kroll develop ed the technique of reduction of the chloride with metallic magnesium which is still the only method of production.

Zirconium had no specific use until 1952. A very small neutron capture cross section (0.18 barn) (1) compared to steel (3.1 barn) as well as an exceptional corrosion resistance in water and steam under pressure ℓ d to the universal use of zirconium alloys as fuel cladding materials for nuclear reactors.

I.2. Zirconium alloys

Many additions have been studied in order to improve the properties of zirconium but very few have led to commercial alloys. The limitations are associated with the following complications:

a. above a few percent of alloying element, complex brittle structures are often formed

b. alloying increases the neutron capture cross section.

Today the main alloys can be classified as:

Alloys having good corrosion properties in water or steam:

*zircaloy 2   1.5% Sn, 0.15% Fe, 0.1% Cr, 0.05% Ni

*zircaloy 4   1.5% Sn, 0.2% Fe, 0.1% Cr, less than

0.007% Ni

*zirconium 2.5% Nb

Alloys having good corrosion properties in CO_2:

*ATR   0.5% Cu, 0.5% Mo

*ZU1   1.8% Cu

*ZU2   2.5% Cu

For chemical applications (hydrochloric acid, nitric acid, organic acids) unalloyed zirconium is preferred.

The high reactivity of zirconium with oxygen, nitrogen and hydrogen led to its use in flash bulbs and getters, (Zirconium alloyed with aluminum, titanium, carbon or nickel).

For the last two decades research on zirconium alloys has greatly increased and their applications range keeps broadening. The use of zirconium as an alloying element in aluminum, magnesium, copper, titanium or molybdenum alloys, super alloys and even steels (2) is an important part of the zirconium market.

I.3. Development of zircaloys

An early study (3) of the corrosion of Van Arkel zirconium in water clearly demonstrated a variability of the quality of the material. The influence of the impurity content and mainly the deleterious effects of

nitrogen, carbon and aluminum were recognized at that time. The "elimination of the disturbed surface layer" (3) by etching in a nitric acid-hydrofluoric acid solution increases the corrosion resistance once the etchant has been well removed.

The results of corrosion tests of sponge zirconium alloyed with tin showed that an optimum addition dependant on the impurity content of the alloy—chiefly nitrogen—could be achieved. For example, an optimum of 2.5% tin was determined for 700 ppm of nitrogen. During corrosion in water, a black oxide is formed in the first stage, followed by flaking and white corrosion products which are usually characteristic of the rapid second stage. The black oxide is more adherent and flaking is markedly retarded when zirconium is alloyed with tin.

The 2.5% tin alloy, called zircaloy 1, showed variations of properties from ingot to ingot and an accelerated corrosion rate for very long exposures to hot water. It is now obsolete. An alloy with small additions of iron, nickel and chromium was called zircaloy 2. It is today the main alloy used for the cladding of nuclear fuel in Boiling Water Reactors (BWR). Zircaloy 3, with a reduced tin content (0.25 to 0.5%) showed local white corrosion and was never produced commercially. Zircaloy 4, very similar to zircaloy 2, with iron replacing nickel, exhibits a lower hydrogen pick up than zircaloy 2 and is preferred in Pressurized Water Reactors (PWR) where the environment is slightly overpressured with hydrogen.

II. REVIEW OF THE LITERATURE

II.1. Introduction

The amount of research work done on zirconium during the last two decades is considerable. The volume of publications on zircaloys could easily fill up several rooms but a single drawer would contain the work done on the studies of zirconium microstructures and on the identification of the phases present. Most publications describe the processing of zircaloys, report on their mechanical properties, the preferred orientation (texture) and the effects of heat treatments, the influence of hydrides and the corrosion properties in various environments at different temperatures.

II.2. Phase diagrams

Phase diagrams of binary zirconium alloys have been studied since 1950. Data on nearly all possible systems are available (4 - 9). Many uncertainties regarding the identified phases still remain today even in the Zr-Sn, Zr-O, Zr-H or Zr-Fe diagrams.

Zirconium has a hexagonal structure (a=3.232 $\overset{o}{A}$, c=5.147 $\overset{o}{A}$) (10) at room temperature (phase α) and it undergoes an allotropic transformation at 865°C. The high temperature structure is body centered cubic (bcc) (phase β). The allotropic transformation $\beta \rightarrow \alpha$ is of martensitic or bainitic type depending on the cooling rate. Alloying drastically modifies this situation. The binary diagrams present on the zirconium rich side a two-phase domain ($\alpha+\beta$). Elements such as oxygen and tin can be considered as α stabilizers (raise the $\beta \rightarrow \alpha$ temperature) and elements such as nickel, iron or chromium as β stabilizers.

The binary diagrams Zr-Sn, Zr-Fe, Zr-Cr, Zr-Ni, Zr-H, Zr-O from Kubaschewski, Von Goldbeck (5) are given in figures 1 to 6. The zirconium-tin diagram (Figure 1) shows that in a 1.5% Sn alloy, tin is in solid solution in the α phase above 500°C and precipitated as Zr_4Sn with a β-W structure (11) below 500°C. The zirconium-iron diagram (Figure 2) indicates a very low solubility of iron in the α phase (0.04 at% at 795°C) and the compound Zr_4Fe precipitates below 795°C for a 0.1-0.3 wt%. Fe alloy. Iron is soluble in the β phase up to several percent in weight. The phase diagram zirconium-chromium (Figure 3) is characterized by one compound $ZrCr_2$ and two eutectics. The maximum solubility in α Zr is 0.49 at% (10.3 wt%) and in β Zr it is 7.5 at%. Precipitation of $ZrCr_2$ is expected below 835°C.

The zirconium nickel diagram shows many intermetallic compounds. The existence of Zr_5Ni (12) has not been confirmed. The solubility of nickel in zirconium has not been determined accurately; it is believed to be very small (Hansen and Anderko (7)) Below 845°C precipitation of Zr_2Ni has been indicated by various authors (5). As oxygen and hydrogen effects have been observed in the present study, the binary phase diagrams Zr-H and Zr-O are included here (Figures 5 and 6). Characteristic data for the binary systems are compiled in Table 1.

Ternary phase diagrams such as Zr-Cr-Sn and Zr-Fe-Sn have also been investigated (13, 14). Tanner (14) indicates the presence of a ternary phase θ between 7 and 8 wt% iron and about 24.5 wt% tin. Sections of the ternary system Zr-Fe-Sn in the zirconium rich corner are given at 700°C, 800°C, 900°C, 1000°C and 1100°C. At 700°C, the
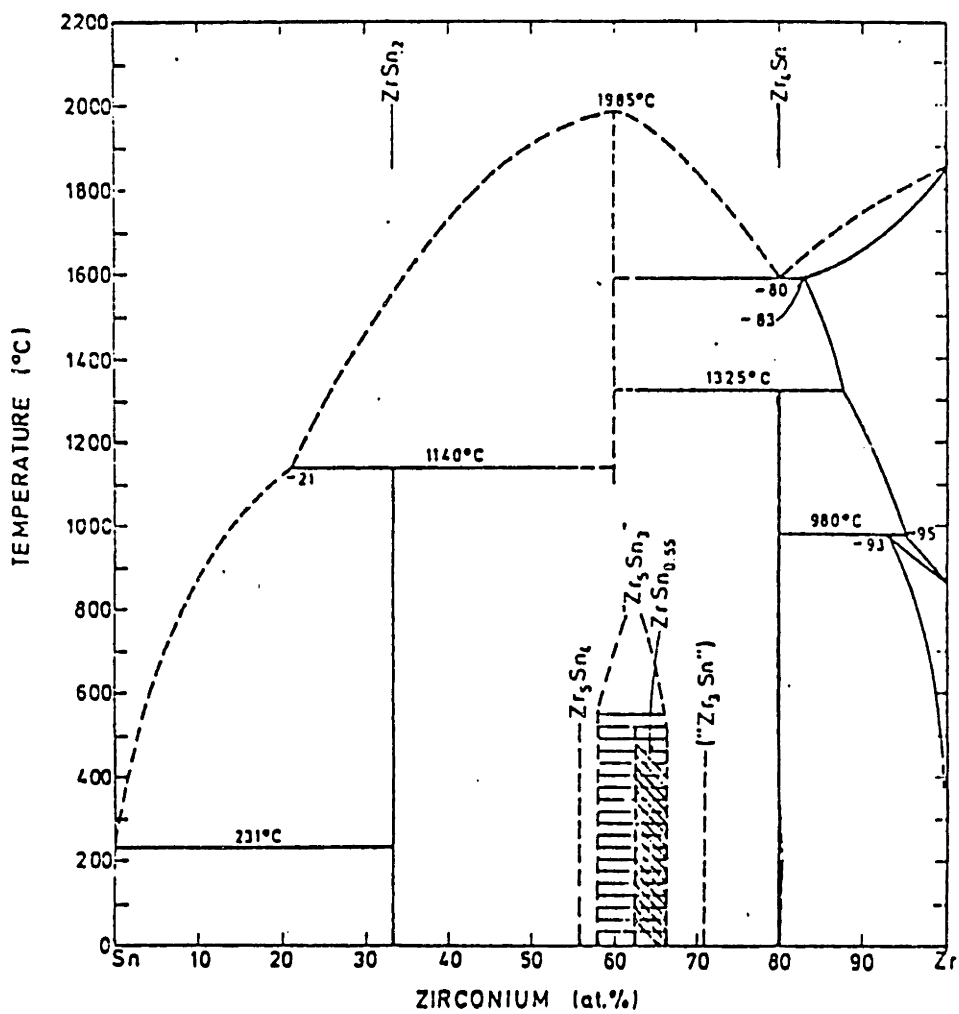
Figure 1: Phase diagram of the system zirconium-tin
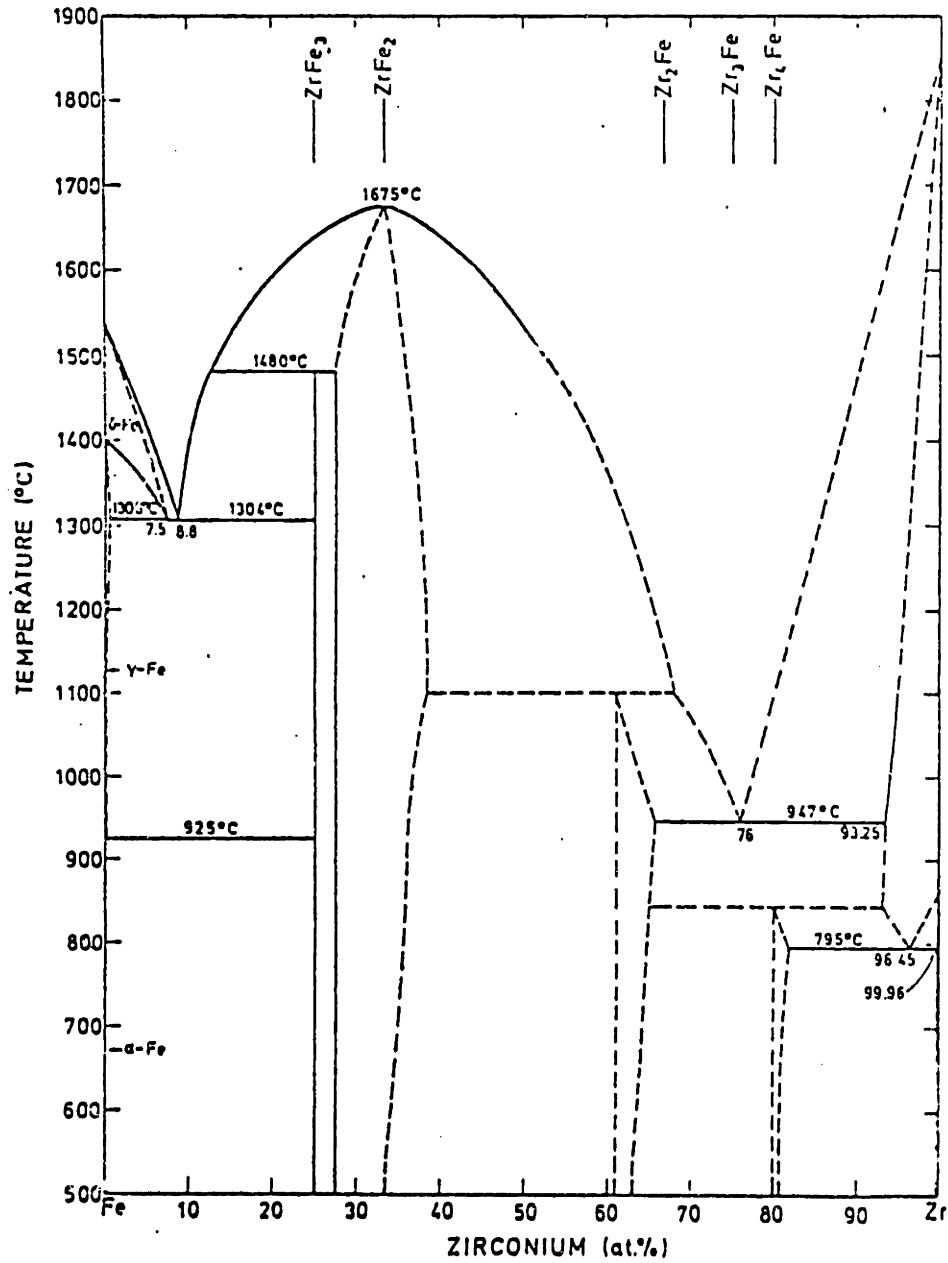
Figure 2: Phase diagram of the system zirconium-iron
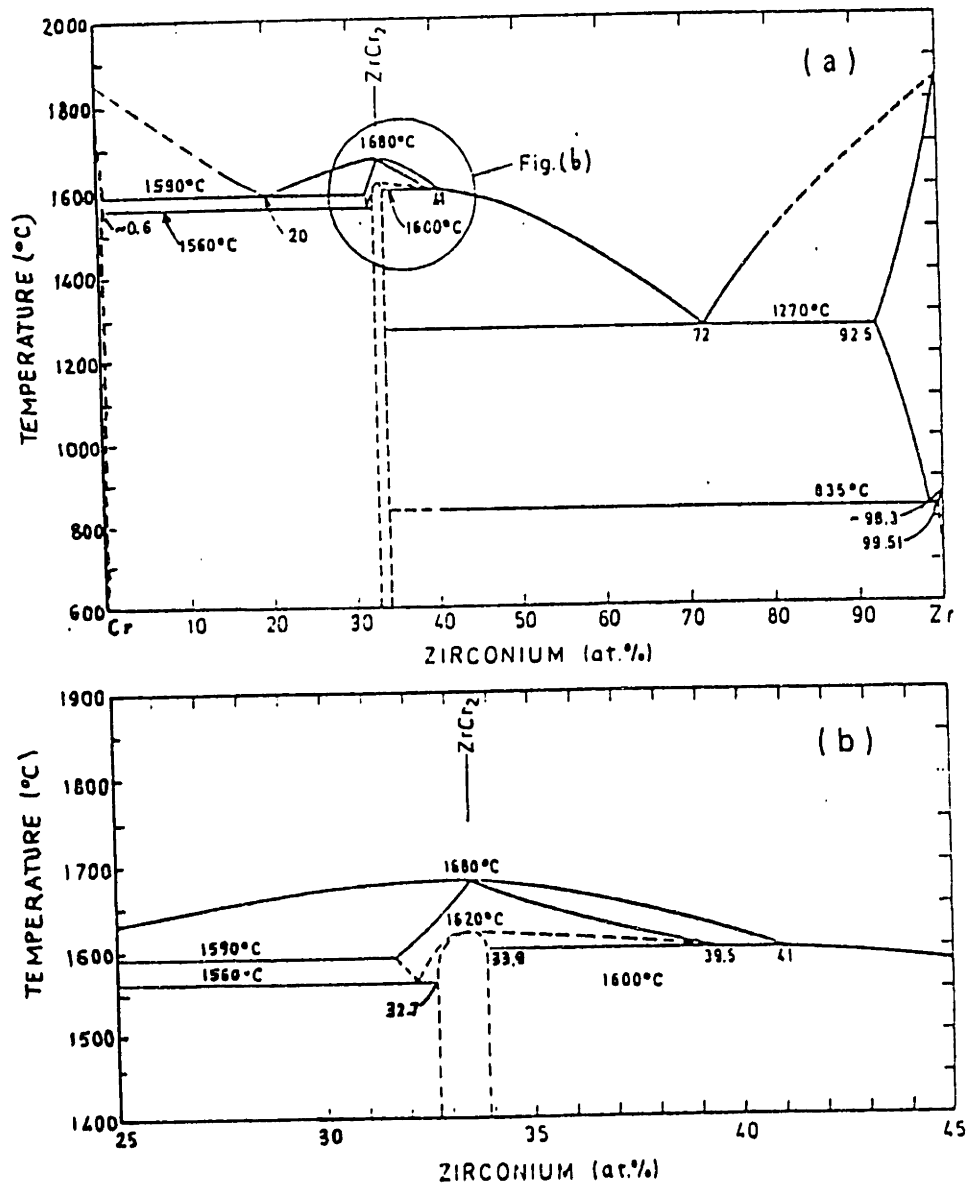
Figure 3: Phase diagram of the system zirconium-chromium
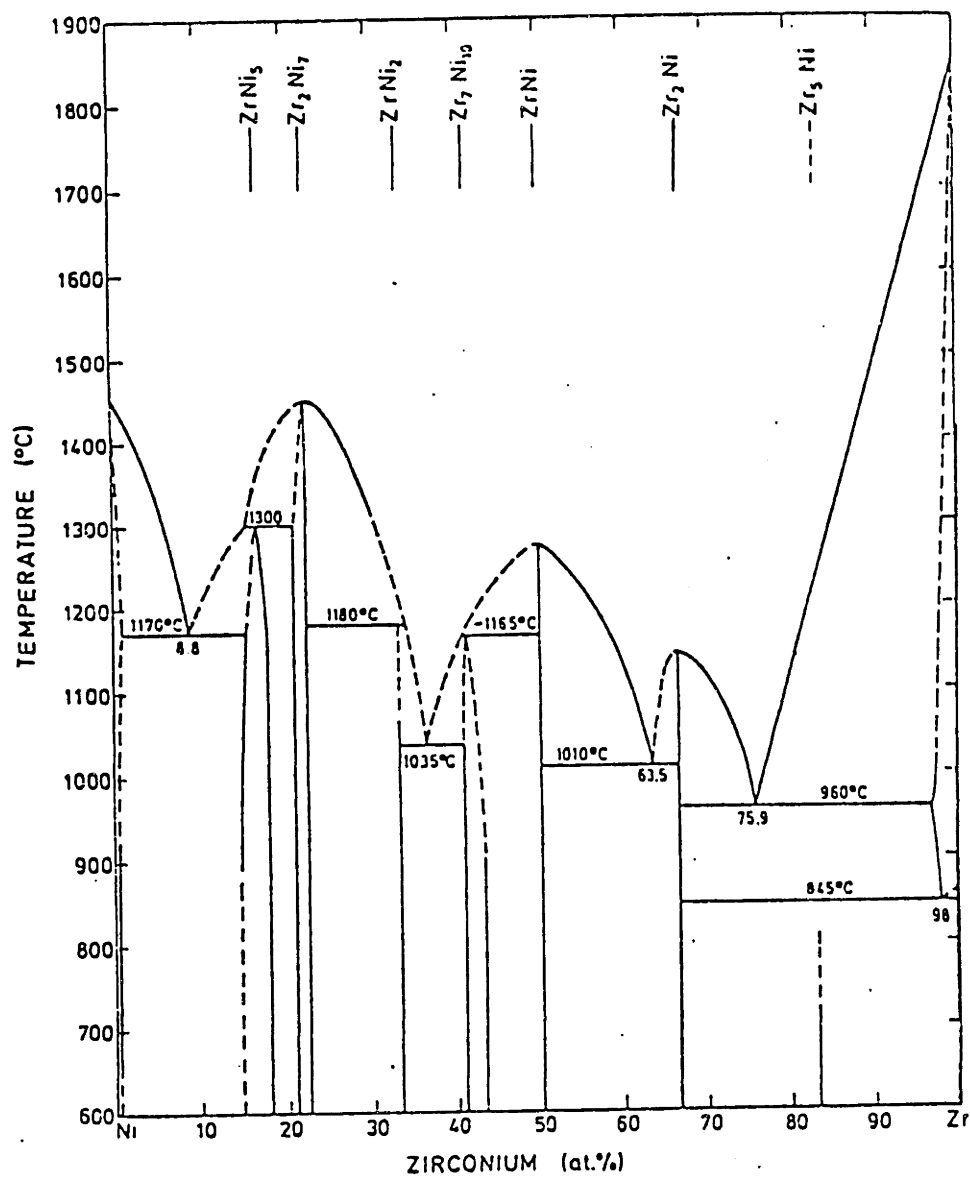
Figure 4: Phase diagram of the system zirconium-nickel
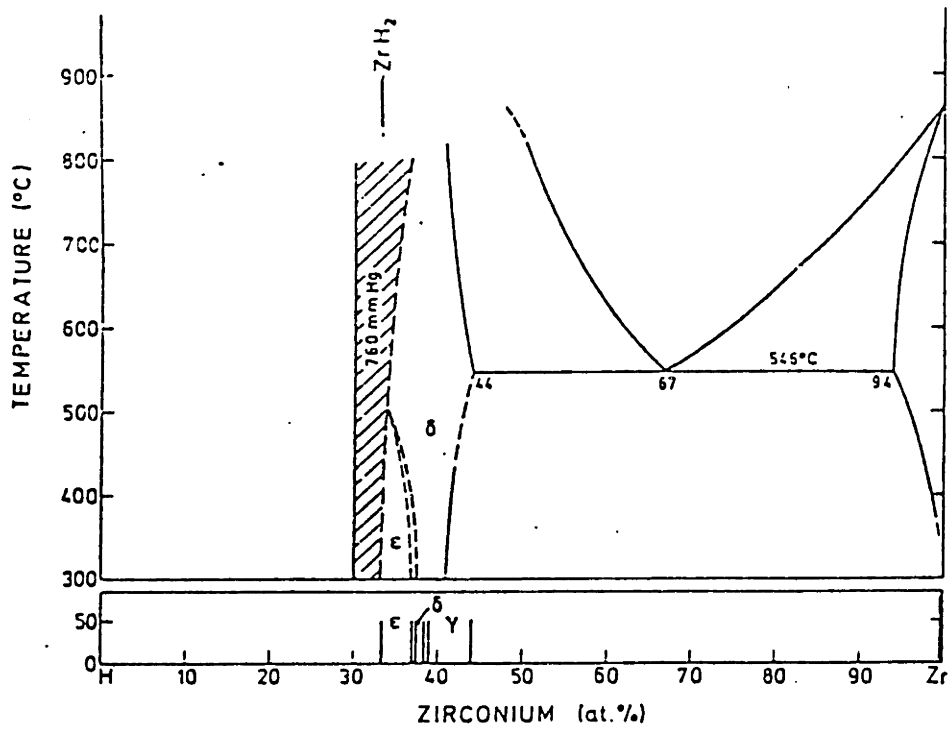
Figure 5: Phase diagram of the system zirconium-hydrogen
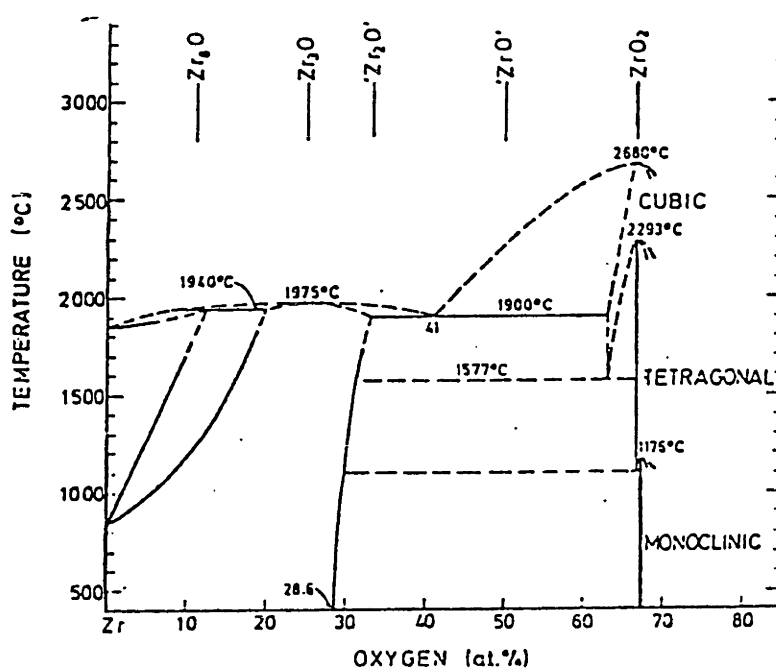
Figure 6: Phase diagram of the system zirconium-oxygen

Table 1 : Binary phase diagram data (6).

Alloying element	Maximum Solubility in β Zr wt%	Eutectic or Peritectic Composition wt%	Temperature °C	Compound or phase in equilibrium
tin	21.0	23.5	1590	$Zr_3 Sn_2$
iron	5.5	16.0	931	$Zr Fe_2$
chromium	4.5	18.0	1300	$Zr Cr_2$
nickel	1.9	17.0	961	$Zr_2 Ni$
oxygen	2.0	?	1940	$Zr_\alpha - O$ (3.75%)
	Maximum solubility in α Zr wt%			
tin	9.0	5.0	980	$Zr_4 Sn$
iron	0.02	2.5	780	$Zr Fe_2$
chromium	very small	1.0	835	$Zr Cr_2$
nickel	very small	1.3	808	$Zr_2 Ni$
oxygen	3.75		1940	Zr_β

θ phase could be present even for very low iron (0.01 wt%) and tin (0.05 wt%) contents. Zr_4Fe was not observed even in the binary Zr-Fe system.

II.3. Metallographic techniques

Different techniques have been used to prepare thin foils of zircaloy for transmission electron microscopy. There are two problems: (a) the formation of hydrides and (b) the preferential etching of inter-metallic particles.

J.B. Vander Sande and Bement have used successfully a chemical rough thinning followed by a final ion milling for zircaloy 4 (15). D.O. Northwood and R.W. Gilbert (16) describe a suitable preparation technique for low hydride production. Instead of using a window technique, as Bedford (17), a jet technique is employed. The thinning is done in two steps: prethinning by chemical polishing in 45% HNO_3 45% H_2O, 5% HF; final thinning by electropolishing in a 4/1 ethyl alcohol: perchloric acid at 240°K under 20V, washing in ethyl alcohol. P. Rao, J.L. Walker and E.F. Koch (18) used a two step electropolishing technique:

first step: 50 ml perchloric acid
             175 ml acetic acid
             100 ml ethylene glycol at 0°C

second step: 190 ml perchloric acid
             760 ml acetic acid at -54°C

Bailey (19) used a single step electropolishing technique. The electrolyte was a 10% perchloric acid 90% glacial acetic acid vigorously stirred and kept cool. The specimen were polished under 20V and washed in distilled water.

II.4. Second phase analysis

The presence of second phase particles in zircaloy has been known for a long time but their chemical composition as well as their crystallographic structure is still uncertain.

Ostberg has determined the TTT curves for zircaloy 2 (20) and has studied the variation of microstructure with heat treatment (21). The transformation study revealed two "noses" on the TTT curve, one at high temperature (about 870°C) for α formation, and one at lower temperature (about 650°C) for precipitation of X, a compound which was later found by Ostberg (22) to contain 5-6 wt% Fe, 0 to 2 wt% Cr, 4 to 9 wt% Ni and 4-5 wt% Sn. P. Rao (18) studied the intermetallic particles in zircaloy 2 and zircaloy 4. The crystallographic structure was determined by selected area electron diffraction and computer simulation. The chemical composition was examined by microprobe analysis on aged specimens. In zircaloy 2, two types of particles are present. One is a chromium-iron-zirconium compound of structure close to $ZrCr_2$ (hexagonal structure a_o = 5.079 Å c_o=8.279 Å). The other type of particle is a nickel-iron-zirconium compound of structure close to Zr_2Ni (tetragonal structure a_o=6.499 Å c_o=5.270 Å). In zircaloy 4, the only particles present were those of the $ZrCr_2$ type which is in agreement with the results of Vander Sande (15) who gives a $Zr_xFe_5Cr_2$ chemical composition based on STEM data. Vitikainen (23) found a $ZrCr_2$ type of particles in a zirconium 0.5 wt% niobium,0.5 wt% chromium alloy called Scanuk 4 but with a f.c.c. structure (a_o=7.195 Å). The two varieties of $ZrCr_2$ have been described by Rostoker (24). According to Rostoker and Pearson (25) the f.c.c. variety is of type $MgCu_2$ with a_o=7.195 kX and stable at high temperature

while the hexagonal variety is of $MgZn_2$ type and stable at low temperature. In Zircaloy 2 Vitikainen (23) found two types of particles (precipitates of type A and B). The particles of type A were round average diameter 0.3-0.6 μm) and of body centered tetragonal structure $(a_o=b_o=6.5 \overset{o}{A}, c_o=5.5 \overset{o}{A})$. Some diffraction spots were missing in particular electron diffraction patterns. The X-Ray analysis with an energy dispersive system showed little nickel and iron. Many particles were partially etched. The particles of type B were smaller (0.1-03 μm) and more elongated. The structure as well as the composition was not determined. Vesaci (26) reported the alternate packing of hexagonal $ZrCr_2$ and face centered cubic $ZrCr_2$ within the precipitates in zircaloy 4.

III. MATERIALS AND TEST PROCEDURES

III.1. Materials

The zircaloy 2 used for this study was supplied by Teledyne Wah

Chang, Albany, Oregon. Cold work stress, relieved tube as received and

plates further annealed by Exxon were examined. The chemical composition of

the tubing (external diameter 0.565 inch, wall thickness 0.05 inch) is given

in Table 2. The level of impurities in zircaloy is kept very low.

Many elements have a very low solubility in α zirconium and can

precipitate, for example: phosphorus, silicon, carbon. Elements such

as nitrogen, titanium, aluminum, silicon and carbon impair the corrosion

properties. Elements as boron, uranium, hafnium and cadmium increase

the cross capture section for thermal neutron, e.g., the cross capture

section of cadmium is 2400 barns. The main impurities in zircaloy 2

are oxygen (1200 ppm), carbon (170 ppm), silicon (40-80 ppm), hafnium

150 ppm) nitrogen (40 ppm) and aluminum (40 ppm). The tube was in a

cold worked, stress relieved condition (stress relieved for about 2 hours

at 500°C). The plate was alternatively cold worked and annealed as

follows:

cold rolled to 0.150 inch

vacuum annealed at 1350°F (730°C) for 2 hours

cold rolled to 0.105 inch

vacuum annealed at 1300°F (705°C) for 2 to 4 hours.

Table 2: Chemical composition of zircaloy 2

alloying element wt %	Specification	tubing	plate Top	Bottom
Sn	1.20 — 1.70	1.50	1.52	1.49
Fe	0.07 — 0.20	0.139	0.14	0.15
Cr	0.05 — 0.15	0.105	0.11	0.10
Ni	0.03 — 0.08	0.053	0.05	0.05
O	0.09 - 0.14	0.131	0.123	0.121
Impurities ppm				
Al	< 75	35	46	41
B	< 0.5	0.2	<0.25	< 0.25
C	< 270	180	170	160
Ca	< 30			
Cd	< 0.5	<0.2	<0.25	<0.25
Cl	< 20	< 5		
Co	< 20	< 10	<10	<10
Cu	< 50	15	13	13
F	< 20			
H	< 25	12	7	11
Hf	< 100	49	63	62
Mg	< 20	< 10		
Mn	< 50	< 25	<25	<25
Mo	< 50	< 25		
N	< 80	47	39	38
Na	< 20			
Nb	< 100	<50		
P	< 20			
Pb	< 130	<50		
Si	< 120	44	87	84
Ta	< 200	<100		
Ti	< 50	< 25	<25	<25
U total	< 3.5	< 0.5	1.8	1.4
V	< 50	< 25	<25	<25
W	< 50	< 25	<25	<25
Zn	< 100			
Fe + Cr + Ni wt%	0.18 — 0.38	0.297	0.30	0.30

III.2. Test procedures

III.2a. Thin foil preparation

Mechanical grinding: Pieces of tube (Figure 7a) were cut to 0.3 inch by 0.3 inch and glued on a brass cylinder with wax. The wax "Rigidax W1 green" melts at 250°F (120°C) and is soluble in trichlorethylene (Figure 7b and c). They were ground with wet SiC paper No.120 -240-360 and 600 on both sides down to 5-6 mils (0.13 mm). The same procedure was followed for 1" x 1" pieces of sheet but the final thickness was 7-8 mils.

Punching: (Figure 7d-e). Three millimeters discs were punched out mechanically. Some of the thickest discs mainly from the sheet presented a small dimple (Figure 7f) due to plastic deformation.

Electropolishing: The jet technique was used with a Fishione apparatus. The electrolyte was 10-20% perchloric acid with 90-80% methanol (in volume) mixed at -30°C. The temperature was maintained below -30°C and down to -65°C by circulation of methanol cooled by a mixture of acetone and dry ice. A potential of 20 to 25 volts was applied for 3 to 10 minutes before the hole was detected. The polishing conditions were very sensitive to experimental parameters such as voltage, jet speed and current transients. The optimum polishing potential was 20 V for the annealed material and 22 V for the stress relieved material. If the potential is too high (26 V and above) or the temperature not low enough (-20°C) pitting occurs and the second phase particles disappear more quickly than the matrix. At very low temperatures (-60°C) a large number of hydrides were formed and -40°C seems to be a good compromise. Since passivation of the metal can occur as demonstrated by a sudden decrease of the intensity of the current (usually ranging

Figure7:Specimen preparation
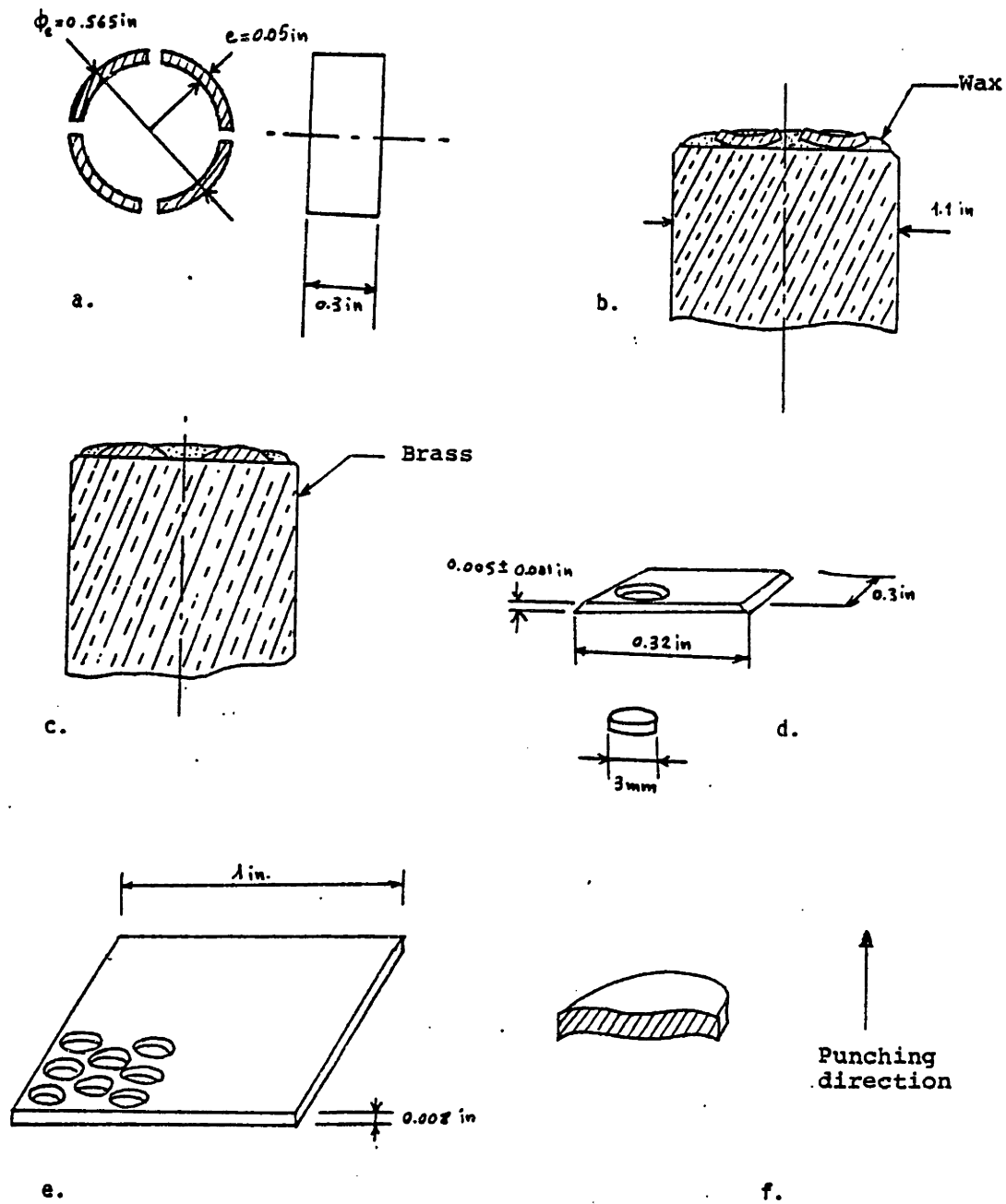
between 15 and 30 mA), the jet strength was set fairly high (position 4 or 5 on the Fishione) and may be a cause of some bending of the foil. An alternative is to raise, momentarily (a few seconds), the voltage and jet speed (7-8 position). The voltage was switched on before the specimen holder was lowered into the polishing bath and switched off when the polished specimen was in the rinse bath. Different solutions were used to rinse the specimen (e.g., distilled water, water with ammonia, methanol). The polished specimens exhibited very different hydride concentrations and it has not been established what exact conditions are required to eliminate the hydrides even if this has been achieved in some specimens. The best foils were obtained with a solution of only 10% perchloric acid. The temperature was about -35°C and the foil was rinsed very quickly after polishing, in water first and then in methanol. A third rinse in distilled water insured a low contamination by the beam during STEM X-Ray analysis.

III.2b. Etching techniques and Extraction replicas

For optical metallography and scanning electron microscopy, pieces of plate were ground with SiC wet paper No.120 and 600 and polished with alumina. The surface was then etched electrochemically under 20V at 0°C with a 10% perchloric acid 90% acetic acid.

Extraction replicas were made in one step. The mechanically polished surface was slightly etched at 0°C by a mixture of 5% hydrofluoric acid, 40% nitric acid, and 55% distilled water.

A film of Carbon (200-500 $\overset{\circ}{A}$ thick) was then deposited under vacuum. The matrix was dissolved using the same solution and the film removed

from the solution as fast as possible. Pieces of film were stretched

flat with the usual alcohol-water technique and placed on copper grids.

Some slightly etched plate samples were kept for SEM investigation.

III.2c. X-Ray analysis

In the SEM and in the STEM the X-Ray analysis was performed with

energy dispersive systems. The spectra were recorded on magnetic discs.

For data analysis and computation, windows of 270 eV width were set on

the main peaks and at different energy levels for background analysis.

Figure 8 shows the repartition of the windows. Characteristic

parameters were chosen to define the spectrums (Table 3). Subsequent

computations were done manually and are tabulated in Appendix D.
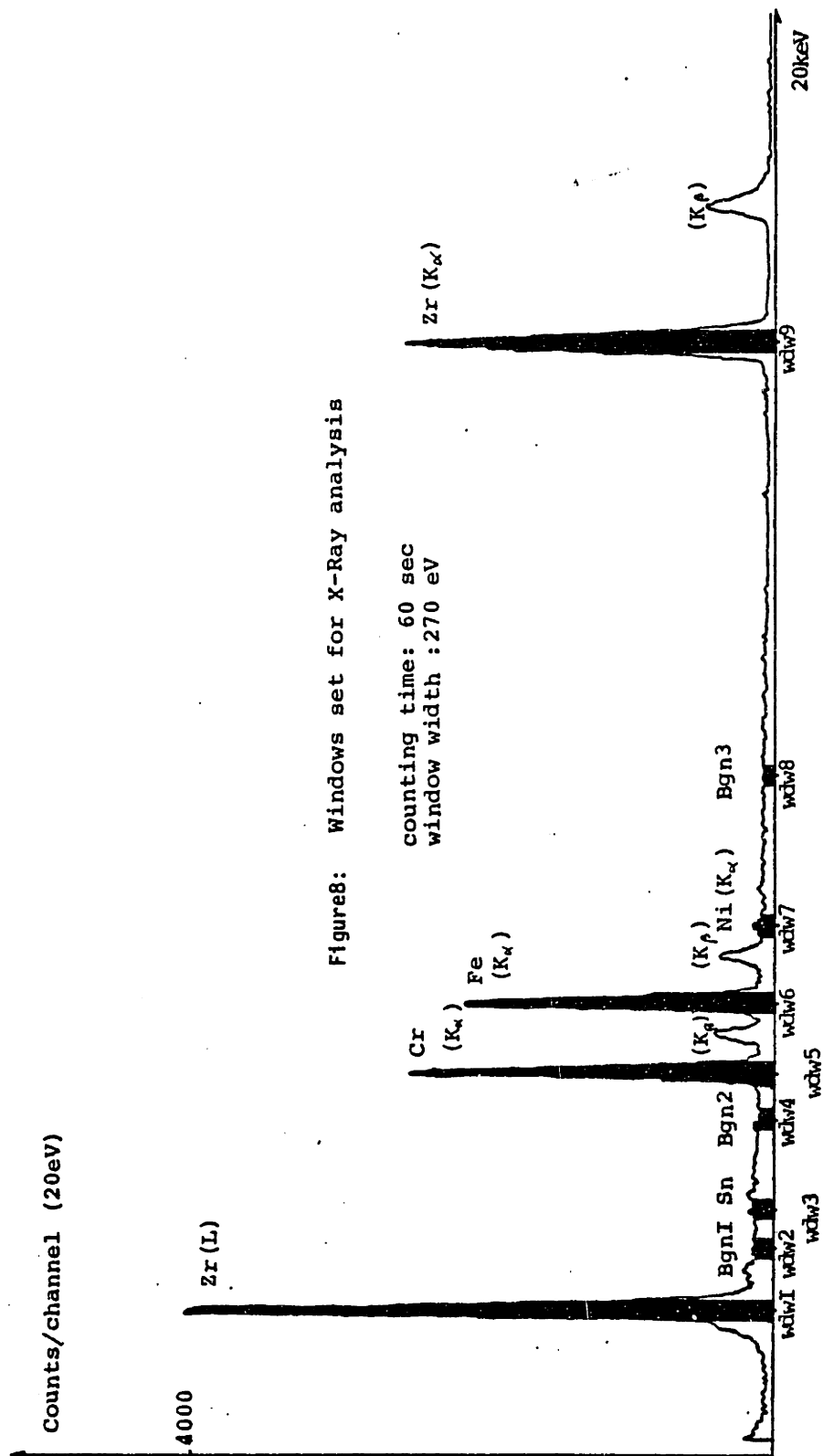
Figure8: Windows set for X-Ray analysis

counting time: 60 sec
window width :270 eV

Table 3 : Characteristic parameters for X-Ray analysis.

window	Region (keV)			description
	from	to	center	
wdw1	1.92	2.18	2.04	L-Ray of Zr
wdw2	2.78	3.04	2.9	Background 1
wdw3	3.34	3.60	3.47	Sn (L-Ray)
wdw4	4.62	4.88	4.75	Background 2
wdw5	5.26	5.52	5.39	Cr (K_α Ray)
wdw6	6.26	6.52	6.39	Fe (K_α Ray)
wdw7	7.34	7.60	7.46	Ni (K_α Ray)
wdw8	9.50	9.76	9.63	Background 3
wdw9	15.58	15.84	15.70	Zr (K_α Ray)

$$BGN = \frac{wdw4 + wdw8}{2}$$

$$Cr = \frac{wdw5 - BGN}{wdw5+wdw6+wdw7-3.BGN}$$

$$Fe = \frac{wdw6 - BGN}{wdw5+wdw6+wdw7-3.BGN}$$

$$Ni = \frac{wdw7 - BGN}{wdw5+wdw6+wdw7-3.BGN}$$

$$Fe/Bgn = \frac{wdw6}{BGN} \qquad L/K = \frac{wdwI}{wdw9}$$

$$Zr = \frac{wdw9}{wdw5+wdw6+wdw7+wdw9-3.BGN}$$

$$Sn/Bgn = \frac{wdw3}{wdw2}$$

IV. RESULTS

IV.1. Optical observation and scanning electron microscopy

The same specimens were observed with a light microscope and with a SEM. The optical observation showed the grain size as well as phases and pits within the grains. The distinction between phases and pits could not be made by optical microscopy.

In the SEM, with a magnification greater than 1000X, particles could be observed. The energy dispersive X-Ray analyses provided their qualitative chemical analysis.

TEM 3 mm discs of cold worked and of annealed zircaloy 2 as well as pieces of electropolished plate were studied with the SEM (model AMR 1000). The surface was irregular and revealed the grain structure. Polishing pits some of which contained "particles", were observed within the grains. The energy dispersive X-Ray analysis revealed, within the pits, regions rich in chromium and iron and less frequently regions rich in nickel and iron. The chemically etched surface of the plate shows the grain size (Figure 9a). Dimples as well as particles can be observed with a magnification of 1000 X (Figure 9a). At higher magnification (Figure 9b), small particles stand out on the matrix surface. The X-Ray analysis, done in the SEM, showed that nearly all the particles present on the surface are chromium and iron rich and only very few contained nickel.

The X-Ray data obtained could not be treated quantitatively and the iron or chromium signal level was always low because the particles were small (0.2-0.3 µm) compared to the analyzed volume (1 μm^3). A typical spectrum of a particle analyzed with the SEM is presented in
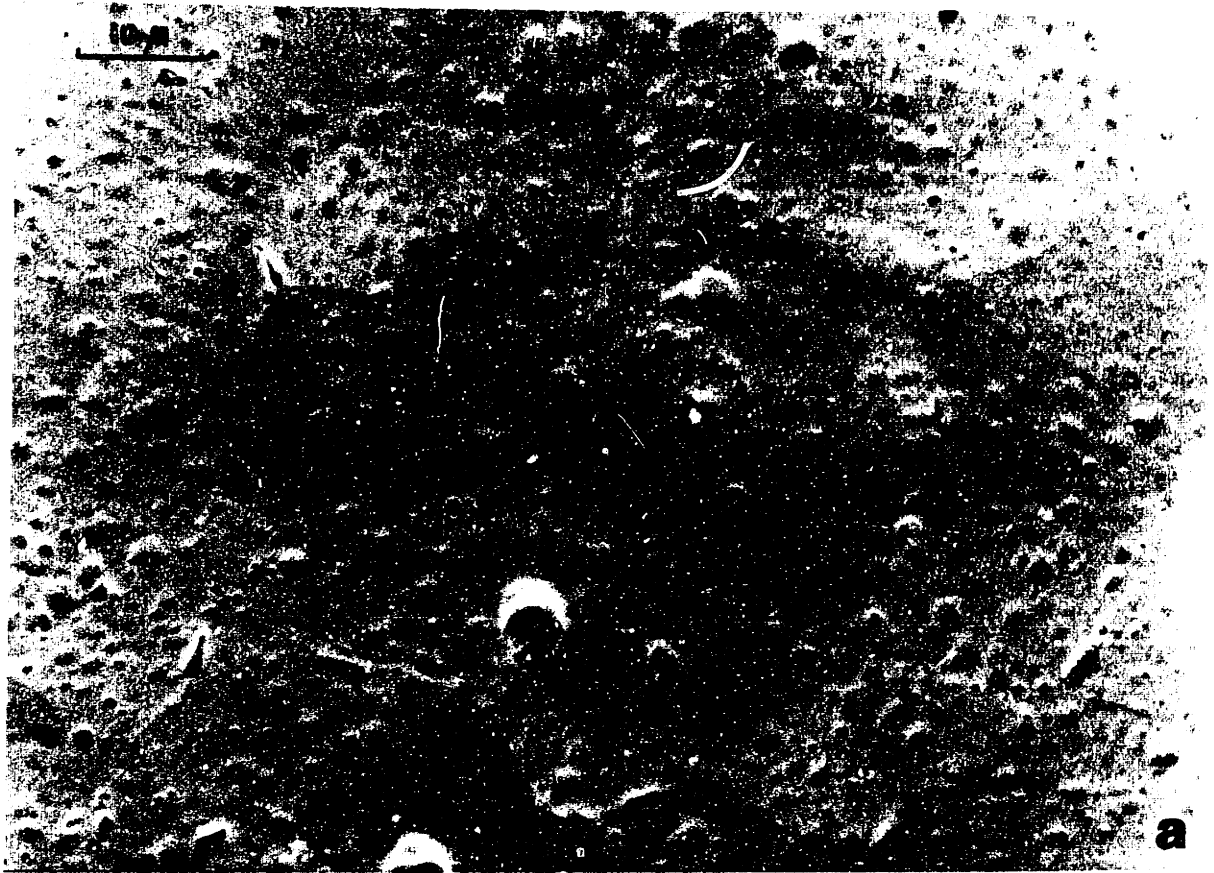
Figure 9 : Scanning electron micrograph of the chemically etched
surface of annealed zircaloy 2.
a) Low magnification view.
b) Chromium rich particles.

10 μ

1 μ

Figure ... electron micrograph ...
surface of annealed circular ...
a) low magnification view.
b) close-up view particles.
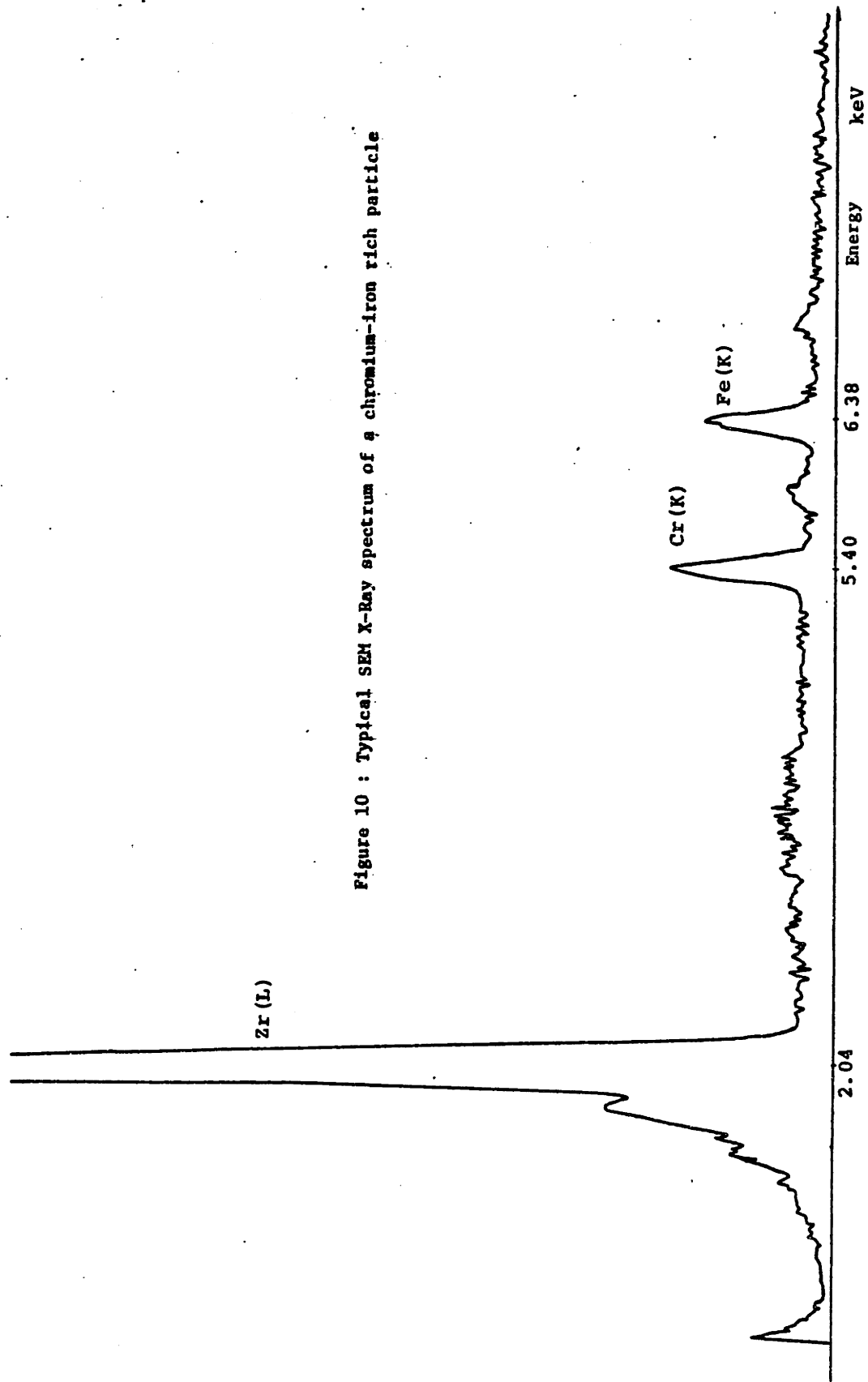
Figure 10 : Typical SEM X-Ray spectrum of a chromium-iron rich particle

Figure 10. All the particles visible in Figure 9b gave a spectrum of this type (chromium and iron).

IV.2. Transmission electron microscopy (TEM)

IV.2a. Introduction

The TEM work was performed on a Jeol model JEM7 microscope for low magnification (20000X) observation and on a Philips model EM300 for structure analysis by electron diffraction. Useful parameters of the instrument were determined by standard methods and are compiled in Appendix E.

IV.2b. General observation

Artifacts: Several artifacts due to foil preparation such as hydrides, slip traces, deformation twins and surface oxide layers were often observed. Bailey (19) studied the hydrides in zirconium thin foils. At low hydrogen concentrations (100-1000 ppm), the hydrides are of the γ tetragonal type. Small round hydrides (0.1 μ) as well as larger platelets (larger than 1 μm) are described. The latter are oriented in the matrix with a (10$\bar{1}$0) habit plane. During their growth, the hydrides can punch out dislocation loops or lines (Figure 11). This (10$\bar{1}$0) habit plane is not in contradiction with the (10$\bar{1}$7) identification made by Westlake (27) for zircaloy 2 and zircaloy 4. The material and the hydrogenation technique used were different.

We observed in zircaloy 2 two types of hydrides. Small round shaped hydrides (0.1-0.2μm) were present on the surface of the foil. Their distribution was uniform within the grains. Often, Moiré patterns and alternate bending of dislocation lines near the surface of the foil were
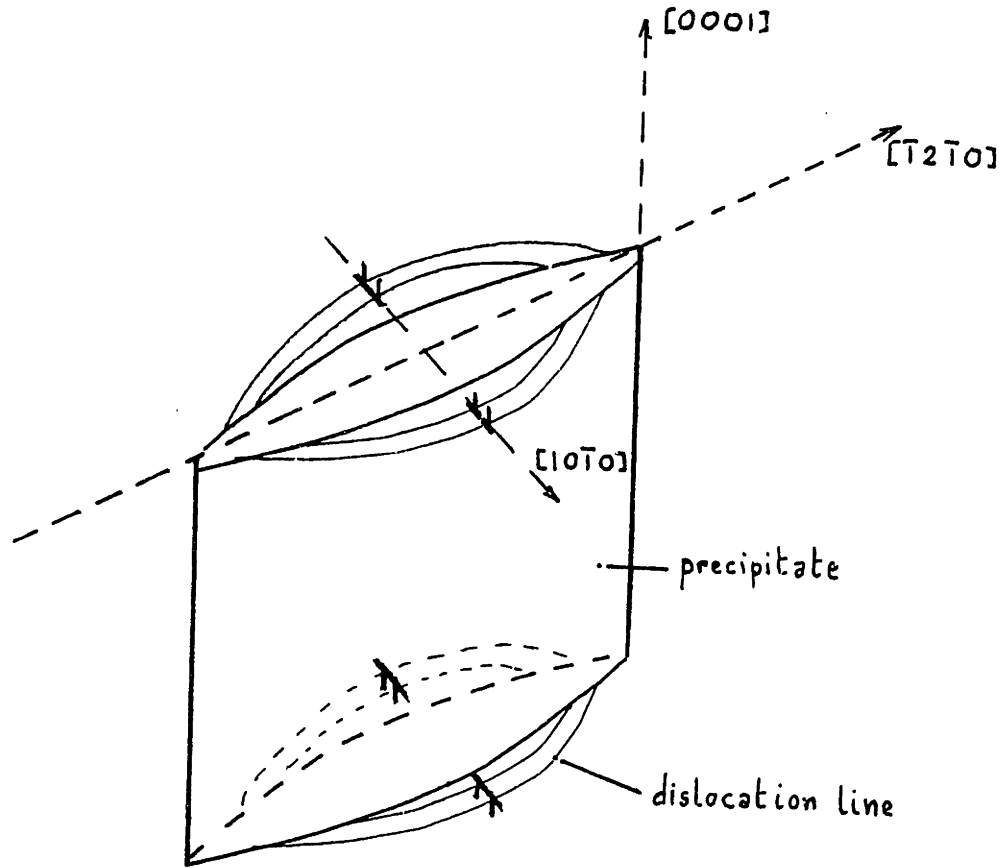
Figure 11 : Illustration of the formation
          of dislocation segments during
          the hydride growth in the [I0.0]
          direction.

0.I-0.2 μm

0.5-I. μm

Matrix contrast

Punched out dislocations

Interaction with
a dislocation at
the surface.

Moiré pattern
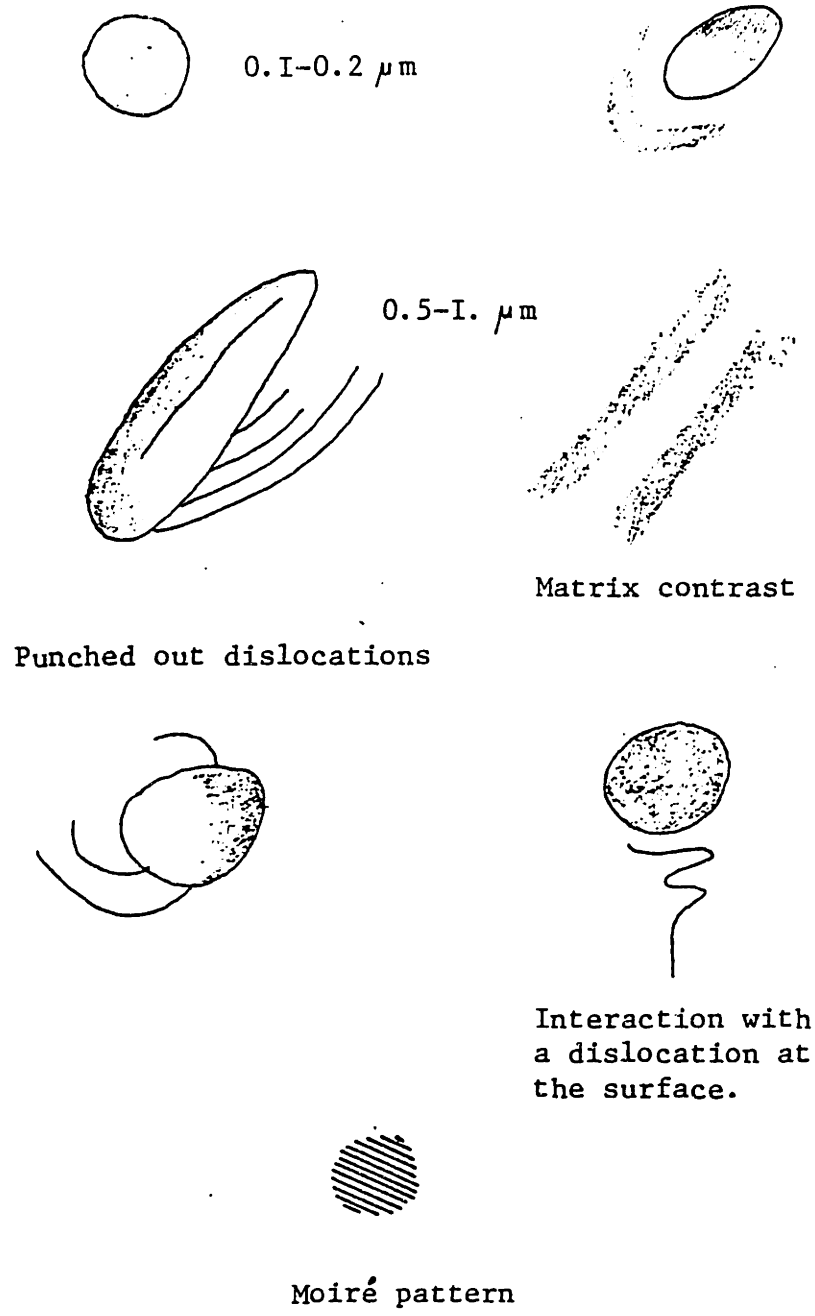
Figure 12:   Illustration of the contrast associated
            with the hydrides.

associated with these hydrides. Fewer but larger needle like hydrides (0.5-1 μm) oriented in three directions were found within the grains.

Large hydrides were often associated with dislocation loops and dislocation lines. The contrast of the hydrides, illustrated in Figure 12, is very dependant on the orientation of the foil. Slip traces due to foil bending and corresponding to prismatic slip were often observed for particular foil orientations. Some specimens exhibited many thin deformation twins (1 μm width) that were probably formed during specimen punching or foil mishandling. On all the specimens, oxidation was responsible for a graininess in the image (100-300 $\overset{o}{A}$ of structure). As a result, the observation of features in the 100-300 $\overset{o}{A}$ range would be very difficult in bright field. In diffraction, elongated additional spots or rings were due to the oxide. The oxide layer, which was oriented differently from grain to grain is probably ZrO_2. Some evidence of the ordered Zr_3O solid solution was found in very thin parts of the specimen. The structure and the X-Ray diffraction analysis of Zr_3O has been described by J. De Buigne (28).

Structure of zircaloy 2: The typical structure of the annealed plate of zircaloy 2 is illustrated by Figure 13. The diameter of the observed grain varied from 4 to 20μ m. The grains were of a regular polygonal shape. Electron diffraction revealed a strong texture. Very few patterns corresponded to poles further than 70° from (0001) and the most common orientations were (0001), ($1\bar{2}13$) and ($1\bar{1}02$). Individual particles as well as clusters were observed within the grains and on grain boundaries. Slip traces, different types of hydrides with punched out dislocation lines, partially etched particles and oxidation

Figure 13 : Transmission electron micrograph of annealed zircaloy 2.
h: hydride. p: particle.
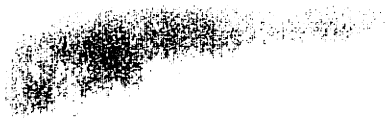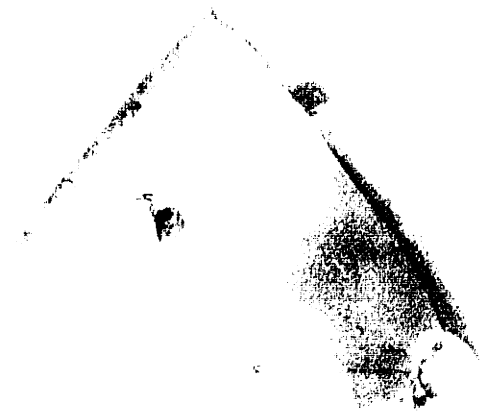
Figure 14 : Transmission electron micrograph of cold worked, stress relieved zircaloy 2.
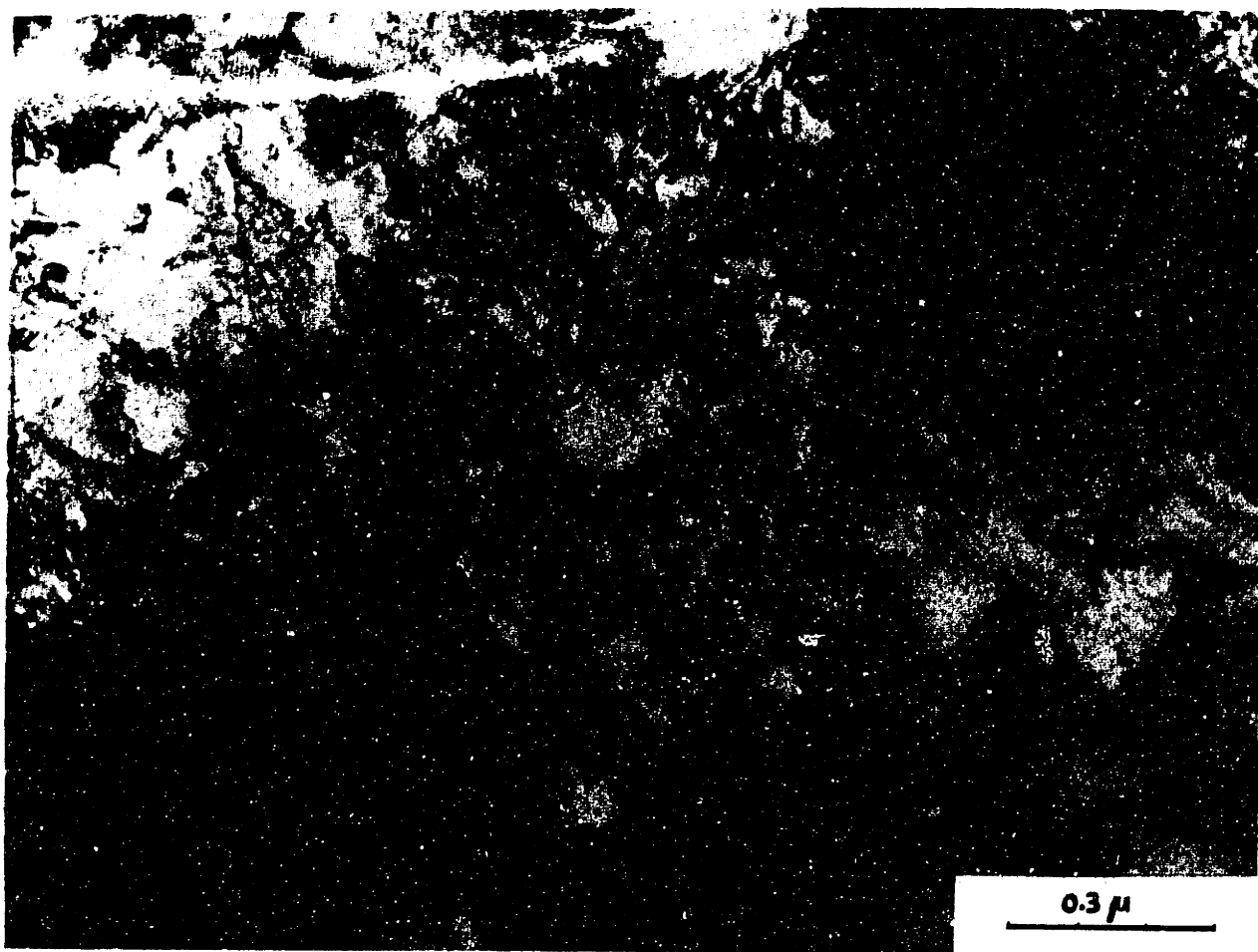
- Figure 15 : Transmission electron micrograph of the dislocation structure in cold worked, stress relieved zircaloy 2.
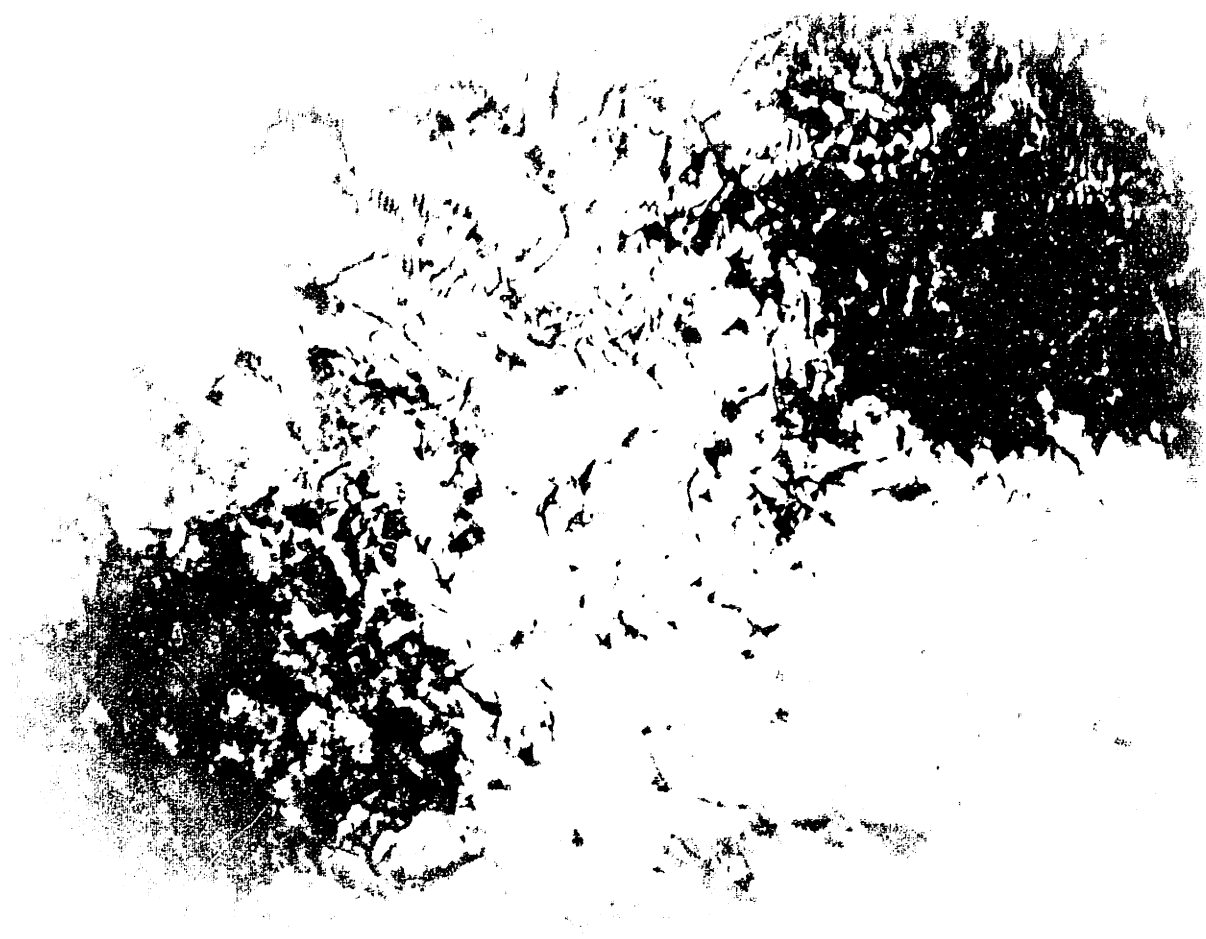
spots can be observed in Figure 13. The foils taken from the cold worked
stress relieved tube exhibited a partially recrystallized structure
(Figure 14). A few dislocation free grains of different sizes (0.5-5 μm),
often in clusters, were observed within a very dislocated background.
Very small particles (0.2μ) were present along with a few particles larger
than 1 μm within the grains and not preferentially at grain boundaries.
Their observation was difficult within the very dislocated structure.
A heterogeneity on a finer scale was observed in the high dislocation
density region (Figure 15) where piled up dislocation lines were common.
The unrecrystallized grains were elongated in a common direction probably
close to the longitudinal axis of the tube.

IV.2c. Second phase particles

Second phase particles were found in the annealed and in the stress
relieved material. Based on their appearance, the individual particles
can be classified basically as six types (Figure 16). The chemical
nature of the particles is the object of part IV.4 of this thesis.
Perfectly spherical particles of small size (0.2-0.4 μm) were very
common in the annealed material (Type 1). These particles normally
diffracted strongly and were not etched preferentially. Some of the
particles of type 1 showed bend contours and appeared as single crystals.
Fewer, larger ovoid particles (0.4-0.6 μm) exhibited a polycrystalline
structure with twins and stacking faults. Particles at grain boundaries
were often of this type (type 2). Very few large ovoid particles
(type 3, 0.6-1 μm), some slightly angular (type 6, 1 μm), were observed.
Most of them were partially etched. Rectangular particles in the 0.2
to 0.6 μm range, exhibiting a thin band structure, probably twins or

Figure 16 :

Different types of intermetallic particles in zircaloy 2

Ni-Fe-Zr particles   type   Cr-Fe-Zr particles

I | 4

0.2-0.4μm   0.2-0.3μm

2 | 5

0.4-0.6μm   0.3-0.6μm

3 | 6

0.6-I.μm   0.6-I.μm

7

0.4-0.8μm
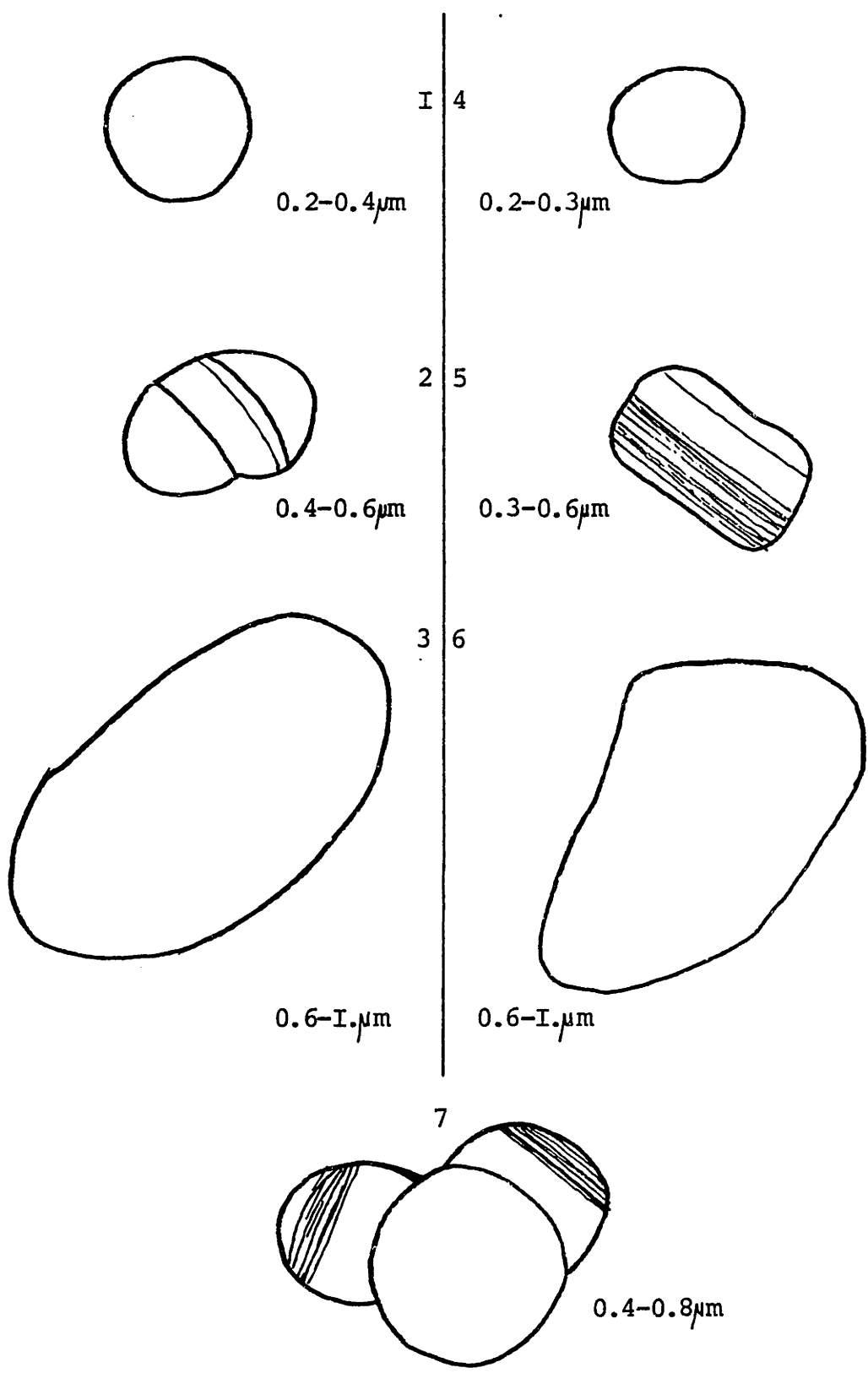
stacking faults for particular orientations of the beam, were very common (type 5). The largest type 5 particles were sometimes partially etched. Some small chromium iron zirconium particles of small size (0.2-0.3 μm) (type 4) can be confused with the nickel iron zirconium particles of type 1 unless electron diffraction or chemical analysis has been investigated. Particles containing chromium are usually more angular than particles containing nickel.

In the annealed plate, many clusters were observed and analyzed in the STEM. Their constitution was well defined: a central particle of type 2 with 1 or 2 type 5 particles attached on different sides. Most of the clusters were of 2 or 3 particles (type 7) and larger ones (5-6 particles) could be decomposed into smaller units of type 7.

The distribution of the individual particles and clusters was uniform. Measurement of the mean spacing between particles is very difficult in TEM because the foil is a wedge, the thickness is not always measurable and many particles were partially or completely etched out. Figure 13 is representative of the material. Particles are between 2 and 5 microns apart. The average size of the particles is 0.3 to 0.4 μm. Nickel rich and chromium rich particles were equally common.

The crystal structure of the particles was determined by electron diffraction. Several patterns were obtained for the same particle in many cases. The lattice spacings were determined assuming a hexagonal matrix with lattice parameters a_o=3.232 Å and c_o=5.147 Å (as pure zirconium). The accuracy of the calculated parameters is no better than 1% even with very careful measurements made directly on the emulsion side of the negative and when the matrix spots used to calculate the camera

Table 4 :   Basic cristallographic data of zirconium compounds.

Composition	Structure	Parameters (in Å)	A.S.T.M. Card N°
$Zr\,Cr_2$	Hexagonal	$a = 5.079$ $c = 8.279$	6-0613
$Zr_2\,Ni$	Tetragonal	$a = 6.499$ $c = 5.270$	13-857
$Zr\,Fe_2$	Cubic ($Cu_2\,Mg$ type)	$a = 7.070$	18-666
$Zr_4\,Sn$	Tetragonal	$a = 6.90$ $c = 11.10$	10-185
$Zr\,(\alpha)$	Hexagonal	$a = 3.232$ $c = 5.147$	5-0665
Hydride γ'	Tetragonal	$a = 4.617$ $c = 4.888$	*
$Zr\,O_2$	Monoclinic	$a = 5.1477$ $b = 5.2030$ $c = 5.3156$ $\beta = 99°23'$	13-307

* Bailey, J.E., Acta Met. 11 (1963) 278

constant were on the same negative.

It has been difficult to index several individual diffraction patterns of particles because of the lack of accuracy of the measurements and because the parameters of the phases are not precisely known.

Our results are in good agreement with the results of PRAO (18). Basic crystallography data for zirconium and zirconium binary compounds are summarized in Table 4. Complementary information is available in the Appendix C of this thesis.

The result of the present study is: (a) Particles of type 1-2-3 have the same tetragonal structure as Zr_2Ni. A particle of type 3, partially etched in the center is presented in Figure 17. A small particle containing chromium is attached on one side. The square (001) electron diffraction pattern included is characteristic of the structure with d_{110} = 4.60 $\overset{o}{A}$ corresponding to a_o=6.51 $\overset{o}{A}$. Other important patterns such as (110), (011), (111) and (012) were observed. (b) Particles of type 4-5-6 have a hexagonal structure and the same crystallographic parameters as $ZrCr_2$ within the accuracy of the measurements. Figure 18 is an example of a particle of type 6, partially etched and showing an internal lamellar structure in dark field (inset d). Figure 19 shows several particles of type 4. The hole on the right side probably corresponds to a particle which has been etched out. Important poles of the hexagonal structure such as (0001), ($1\bar{2}10$), ($10\bar{1}0$), ($1\bar{2}13$) or ($10\bar{1}2$) were observed. The cluster shown in picture 20 is of the type 7 previously described. The central particle is of the type Zr_2Ni and two chromium rich particles of the $ZrCr_2$ type are attached. The type 5 particles were twinned perpendicularly to the
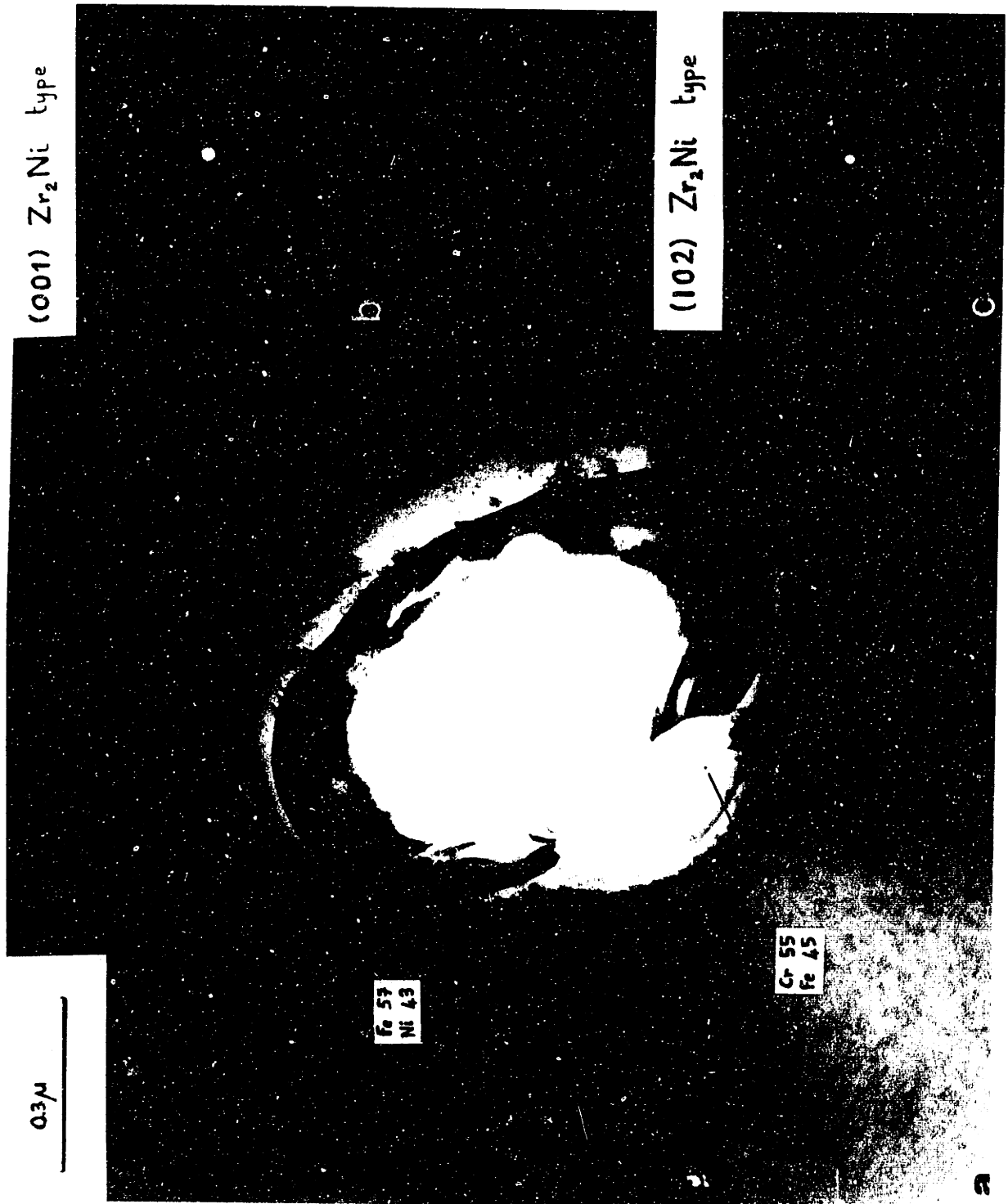
Figure 17 : Transmission electron micrograph of a nickel-iron
rich particle in annealed zircaloy 2.
a) Bright field image.
b) (001) electron diffraction pattern.
c) (102) electron diffraction pattern.

48.
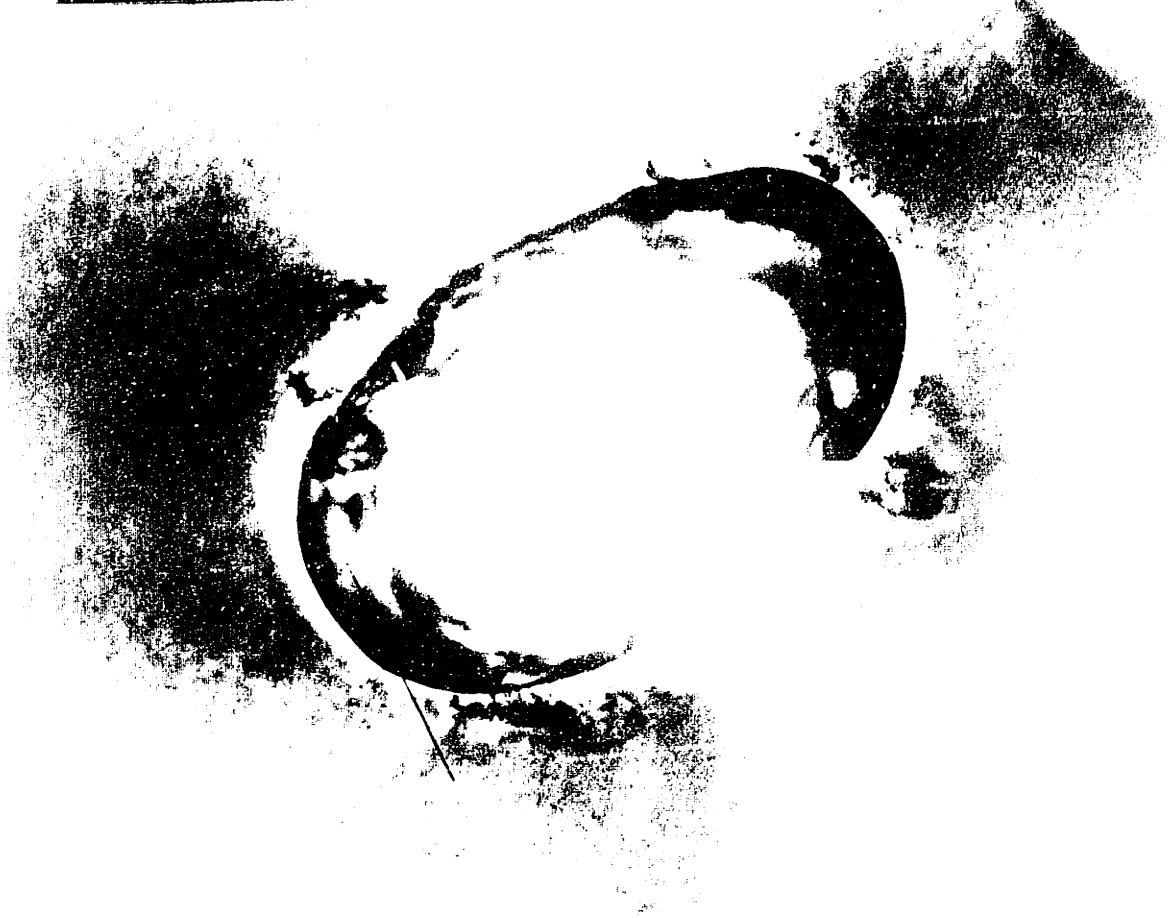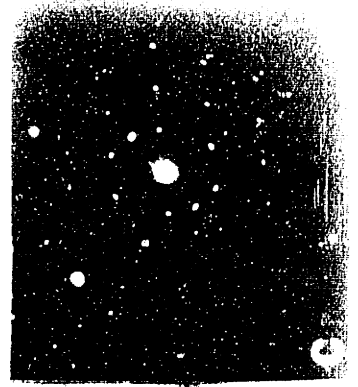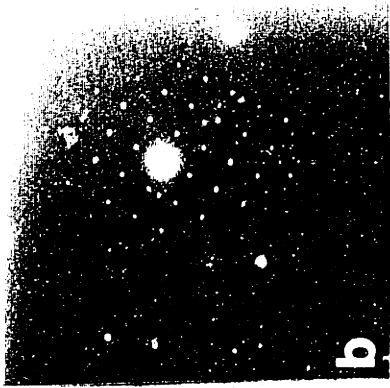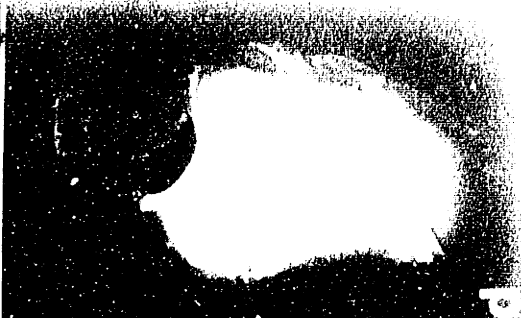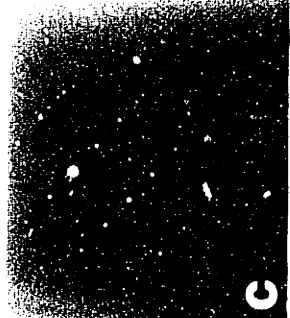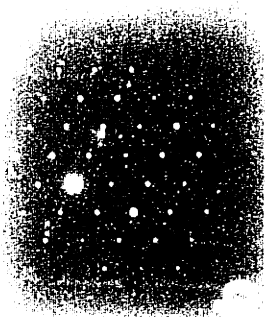
Figure 18 : Transmission electron micrograph of a chromium-iron
rich particle in annealed zircaloy 2.
a) Bright field image.
b) (1$\bar{2}$13) electron diffraction pattern.
c) ($\bar{5}$416) electron diffraction pattern.
d) Dark field image corresponding to a (20$\bar{2}$1) reflexion.
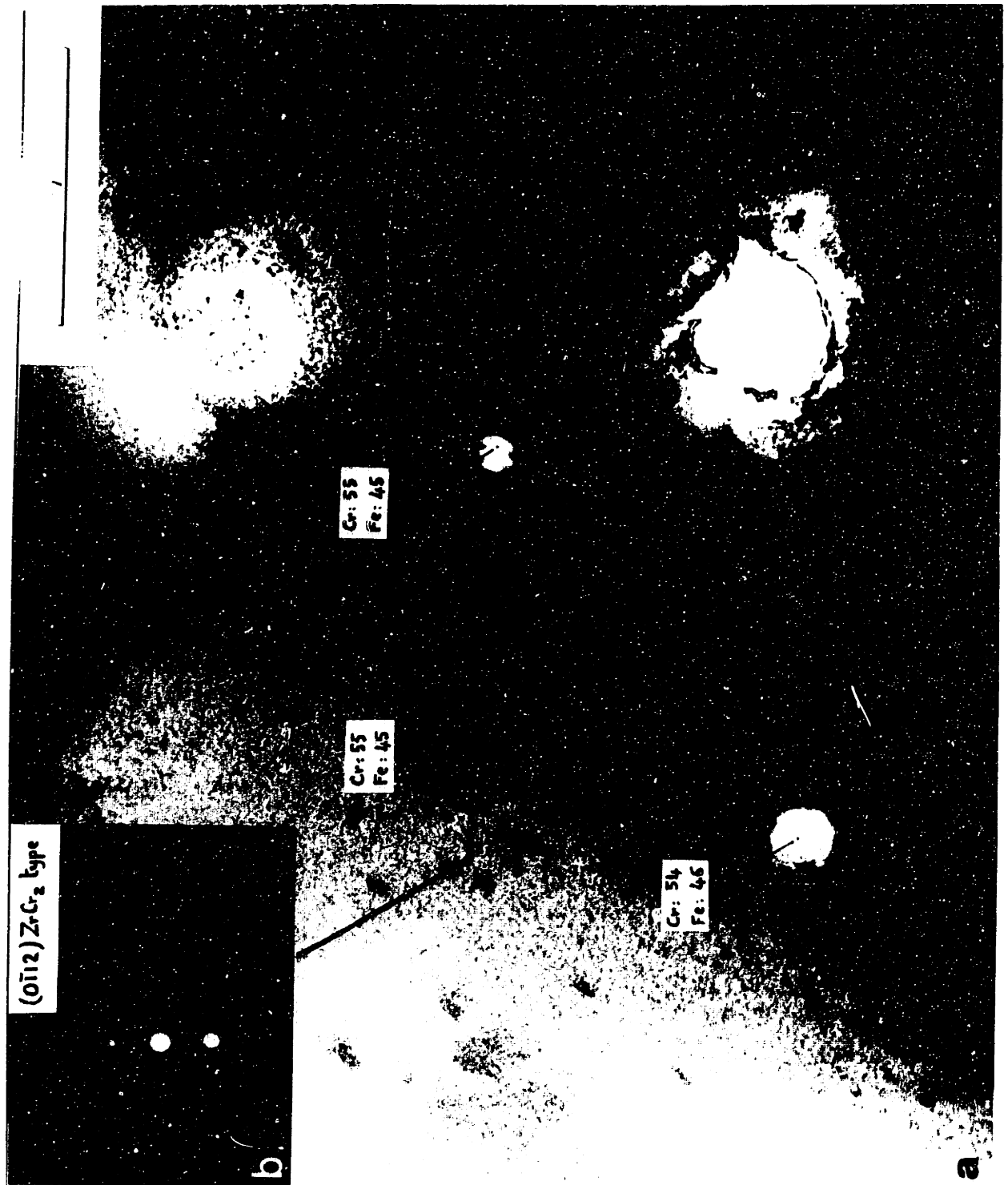
49.

Figure 19 : Transmission electron micrograph of chromium-iron
rich particles in annealed zircaloy 2.
a) Bright field image.
b) (0$\bar{1}$12) electron diffraction pattern.
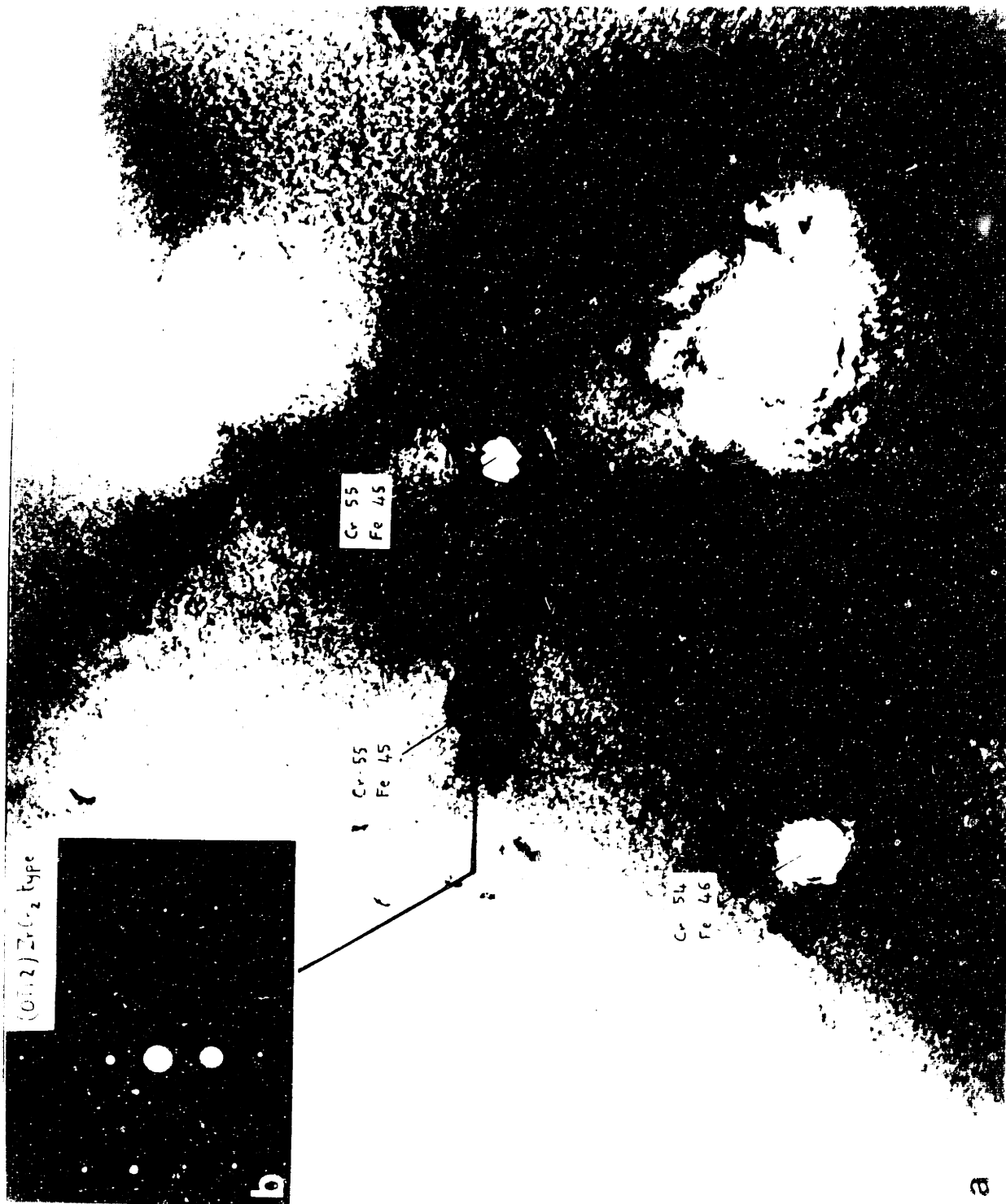
49.

Figure 19 : Transmission electron micrograph of chromium iron rich particles in annealed zircaloy 2.
a Bright field image.
b Diffraction from (0.2)ZrCr₂ type.
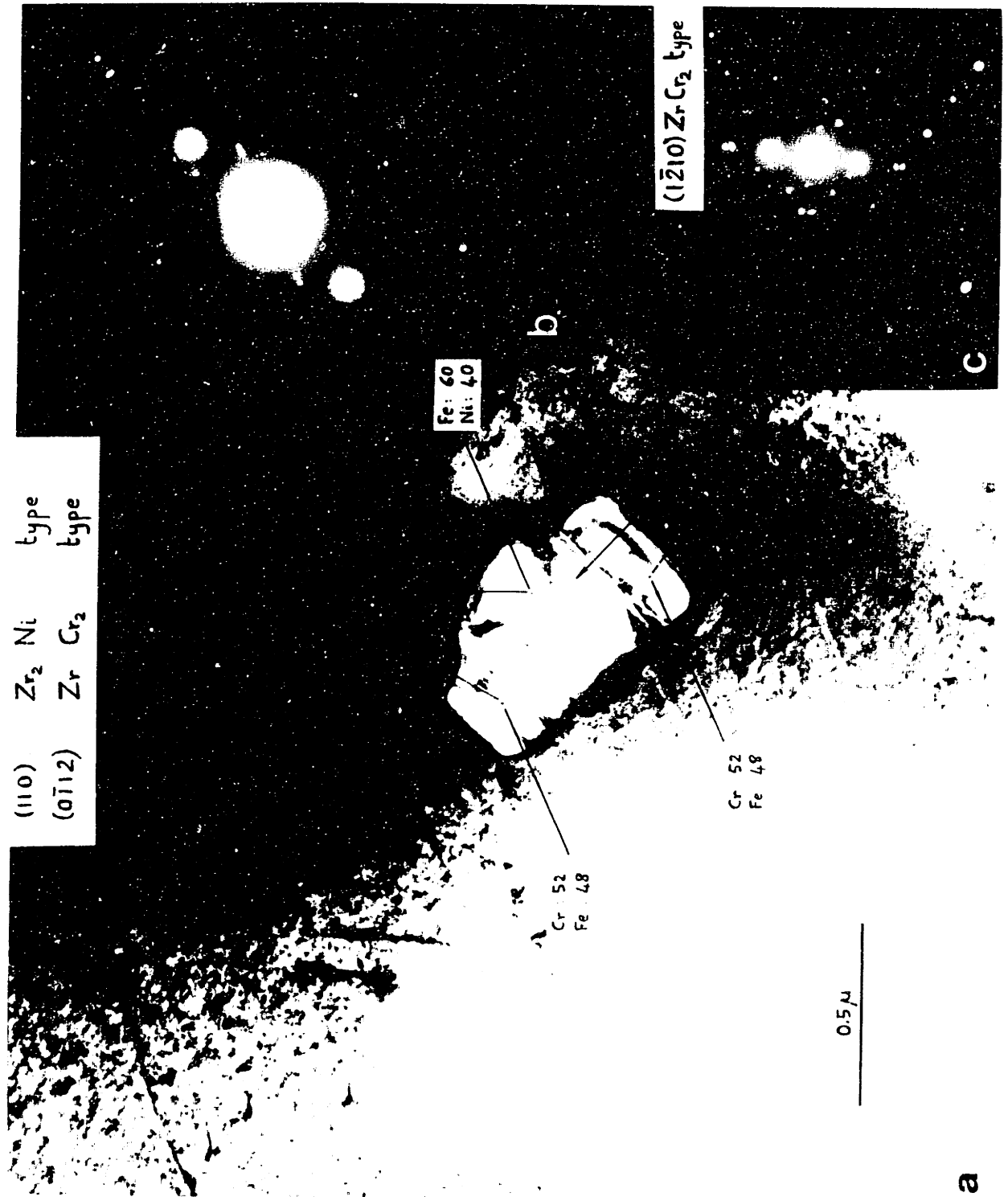
Figure 20 : Transmission electron micrograph of a cluster
of intermetallic particles in annealed zircaloy 2.
a) Bright field image.
b) (110) and (0$\bar{1}$12) electron diffraction patterns.
c) (1$\bar{2}$10) electron diffraction pattern.

0.3 μ
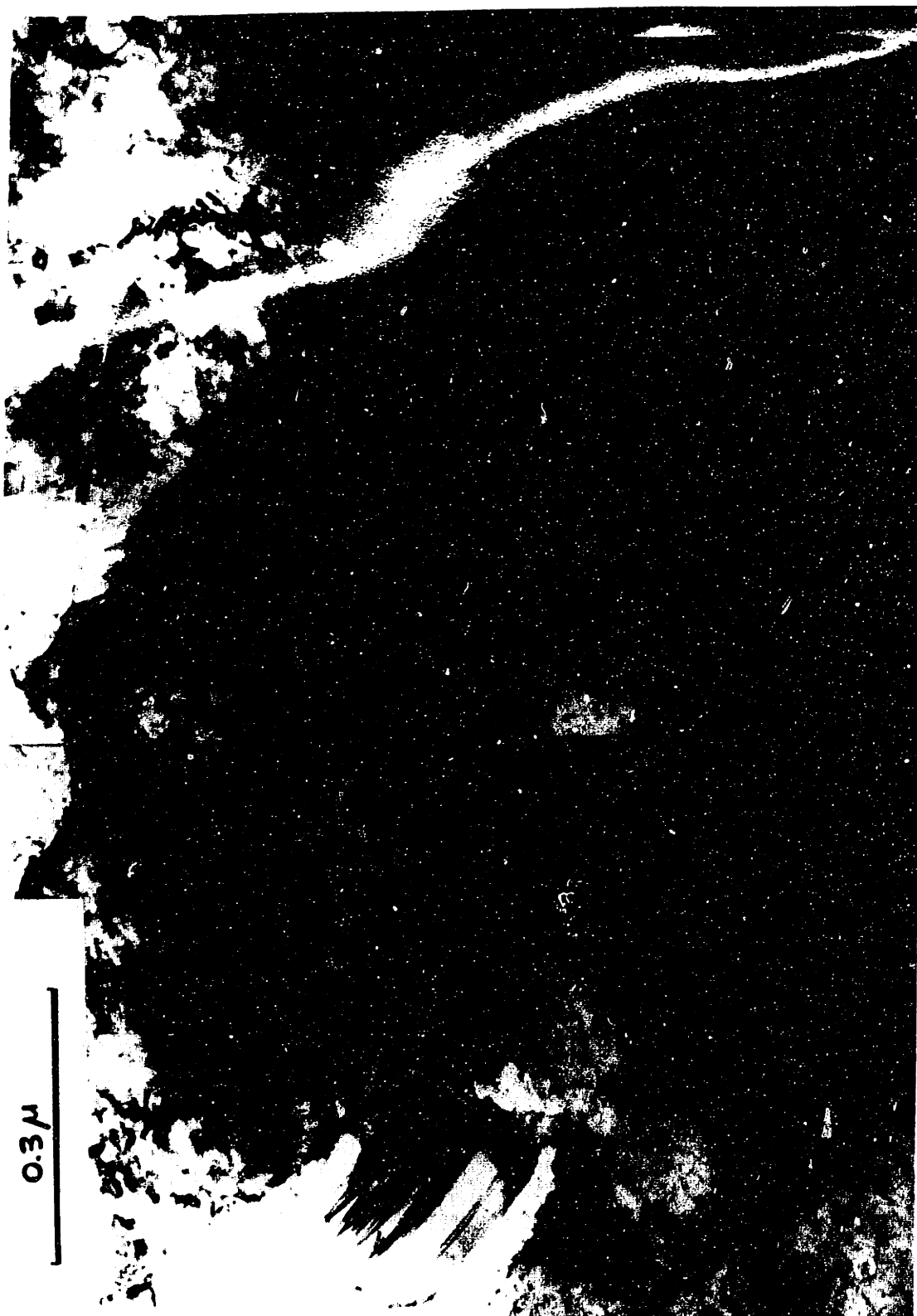
Figure 21 : Transmission electron micrograph of intermetallic
particles in cold worked, stress relieved zircaloy 2.
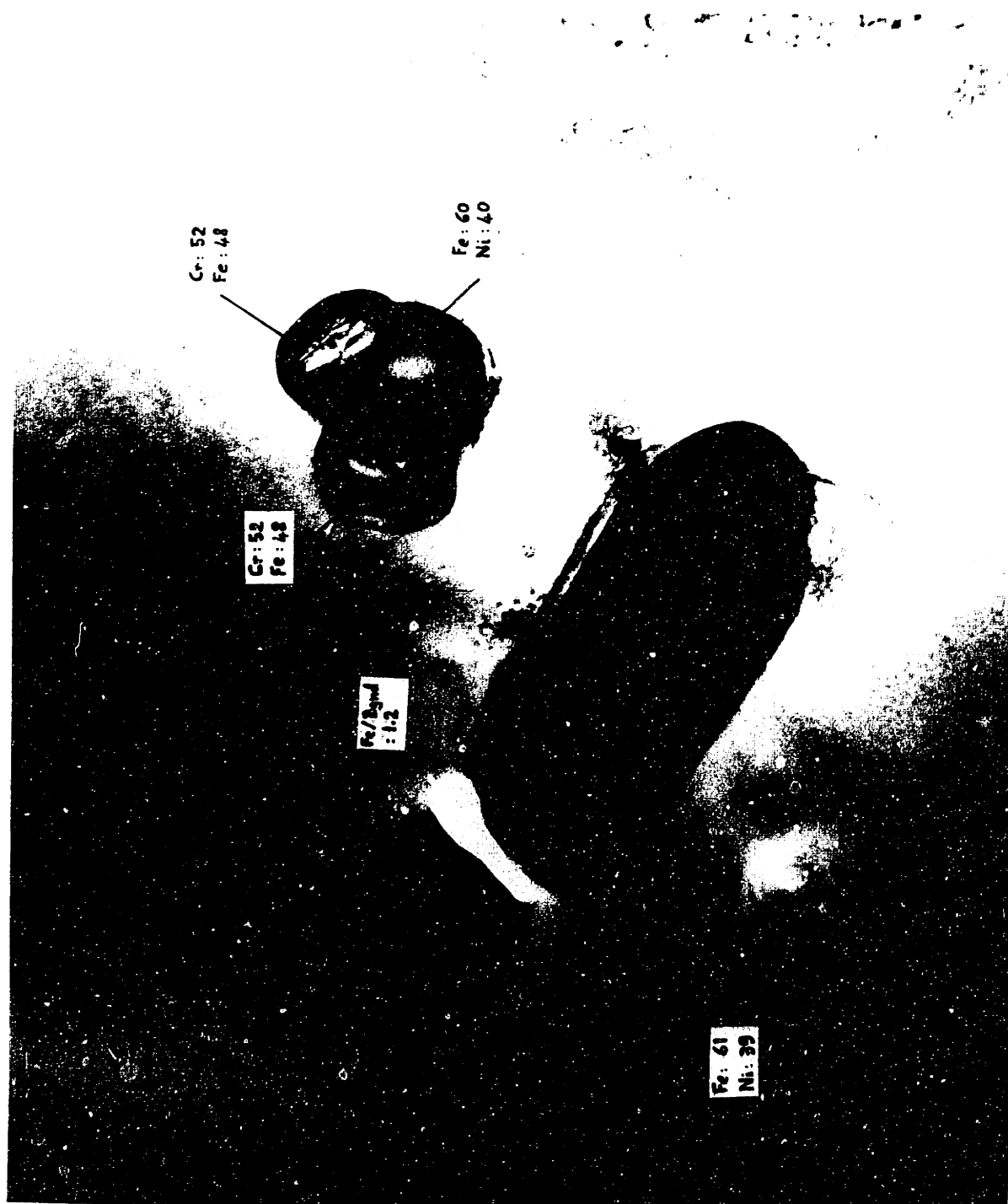
Figure 22 : Transmission electron micrograph of intermetallic
particles close to an inclusion in annealed zircaloy 2.
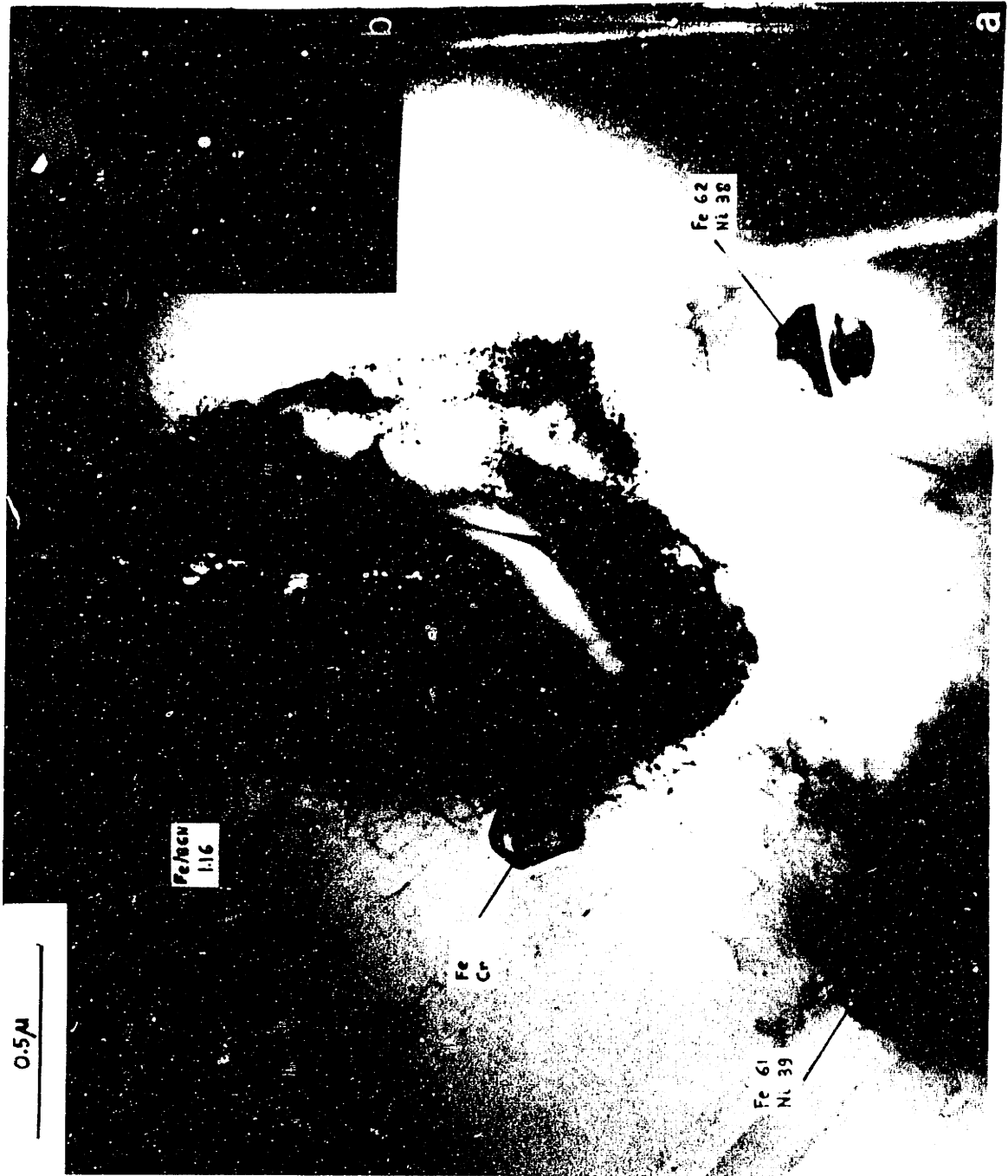
Figure 23 : Transmission electron micrograph of a Zr_3Si inclusion
in annealed zircaloy 2.
a) Bright field image.
b) (011) electron diffraction pattern.
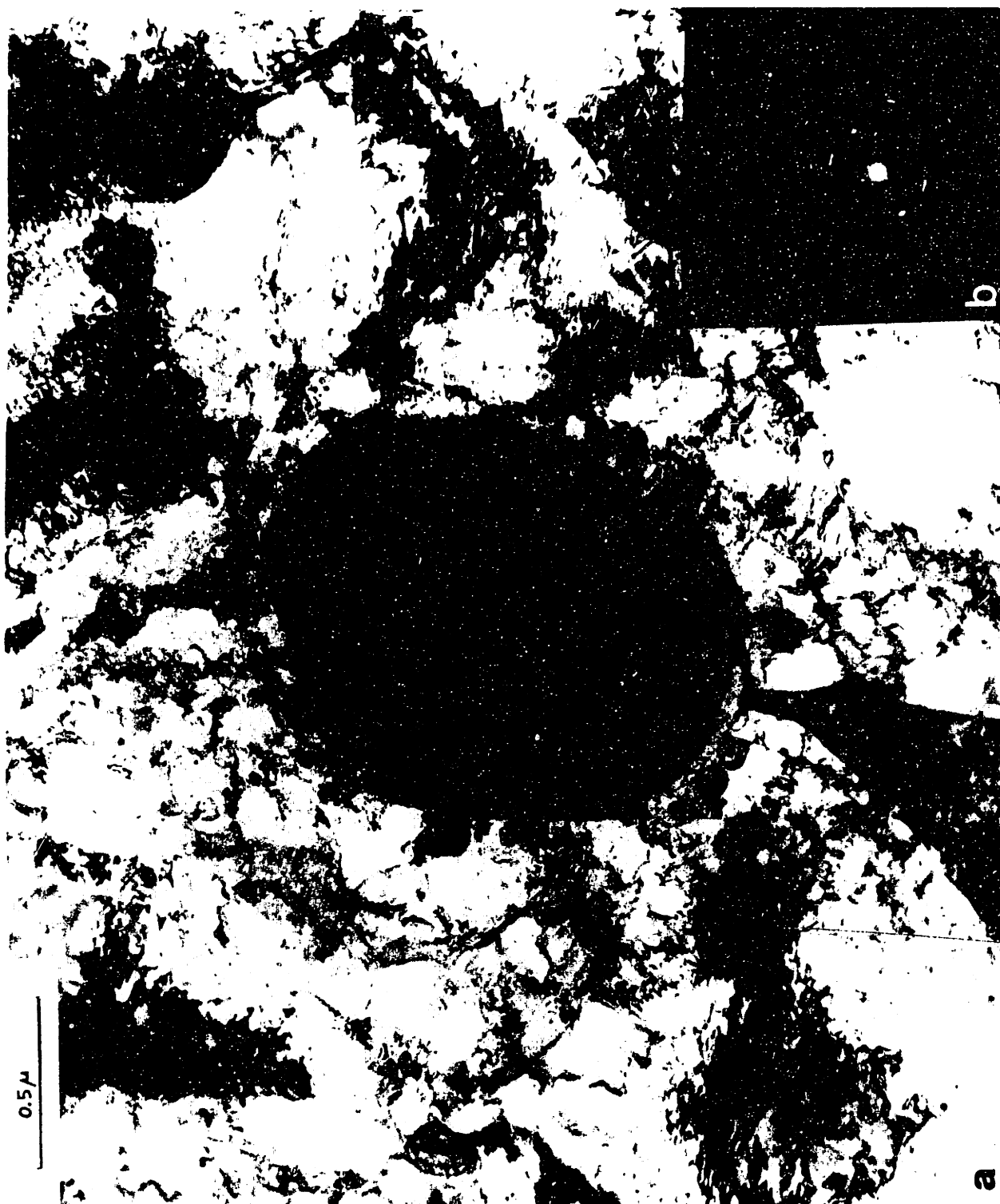
Figure 24 : Transmission electron micrograph of a Zr_3Si inclusion
in cold worked, stress relieved zircaloy 2.
a)Bright field image.
b) (013) electron diffraction pattern.

Figure 24 : Transmission electron micrograph of a Zr$_3$Si inclusion
in cold worked, stress relieved zircaloy 2.
a) bright field image.
b) (013) electron diffraction pattern.

<0001> direction and, in diffraction, streaks were often observed in

this direction. For the cluster of Figure 20a, it was possible to show

that the two particles have a strong crystallographic relationship, two

sets of planes being parallel. The cold worked stress relieved material

contains the same types of particles but their structures have not been

determined by electron diffraction. The same type of particle was

of smaller average size in the cold worked,stress relieved material than

in the annealed material. Figure 21 shows a type 1 and a type 5 particle

next to a dislocation network.

IV.2d. Inclusions

Large inclusions (1-2 μm), often elongated, were observed in annealed

and in stress relieved zircaloy 2. They were not very common (about one

per thin foil in the annealed plate). The inclusions were often too

thick to give good electron diffraction patterns, however a tetragonal

structure with a_o=11 $\overset{o}{A}$ and c_o=5.5 $\overset{o}{A}$ fitted nearly all the patterns. Such

a structure has been reported for silicides of the type Zr_3Si by

Schubert (29) and was suggested by D. Charquet (30). Two such inclusions

are showed in Figures 22 and 23. The cluster of type 7 on Figure 22

presents a slight Moïré pattern corresponding to a hydride. Very few

intermetallic particles were observed on the inclusions but they are

often present in the neighboring matrix. The observed inclusions were

more elongated in the annealed material than in the stress relieved

material. Figure 24 shows the slight misorientation between two components

of a Zr_3Si type inclusion in the stress relieved material.

IV.3. Scanning transmission electron microscopy

In order to determine the chemical nature of the precipitates in zircaloy 2, a Vacuum Generators HB5 dedicated STEM was used. It provides a very good spatial resolution for X-Ray analysis (electron beam smaller than 20 Å in diameter).

One can have a good idea of the repartition of the particles by looking at the annular dark field image in the STEM (Figure 25). This imaging mode was also useful when looking at particles in thick regions of the foil. For X-Ray analysis, the beam was centered on the particle of interest. A counting time of 15 to 120 seconds was enough to provide accurate information. The spectra were recorded and characteristic indices were calculated as described in Part III.2c. of this thesis. Chemically, two very distinct types of intermetallic particles were found. (a) Particles of type 1-2 and 3 showed only nickel and iron besides zirconium. Figure 26 shows a typical spectrum from a nickel-iron rich particle. The statistics demonstrate a very precise chemical composition for these particles. A Fe/Ni ratio of 60/40 can be inferred from Figure 27. The scatter of the Zr index should be considered as a matrix effect. However all the data are above 0.5.

(b) Particles of type 4-5-6 showed very similar results. They are composed of chromium, iron and zirconium (no tin or nickel). The Fe/Cr ratio of 45/55 is fairly constant. An example of spectra and statistics are given in Figures 28 and 29. The scatter of the Zr index is very large with a lower limit of 0.22. The extraction on carbon films is described in Part III.2b. of the thesis. The analyses in the STEM showed that the nickel rich particles were not extracted. All the
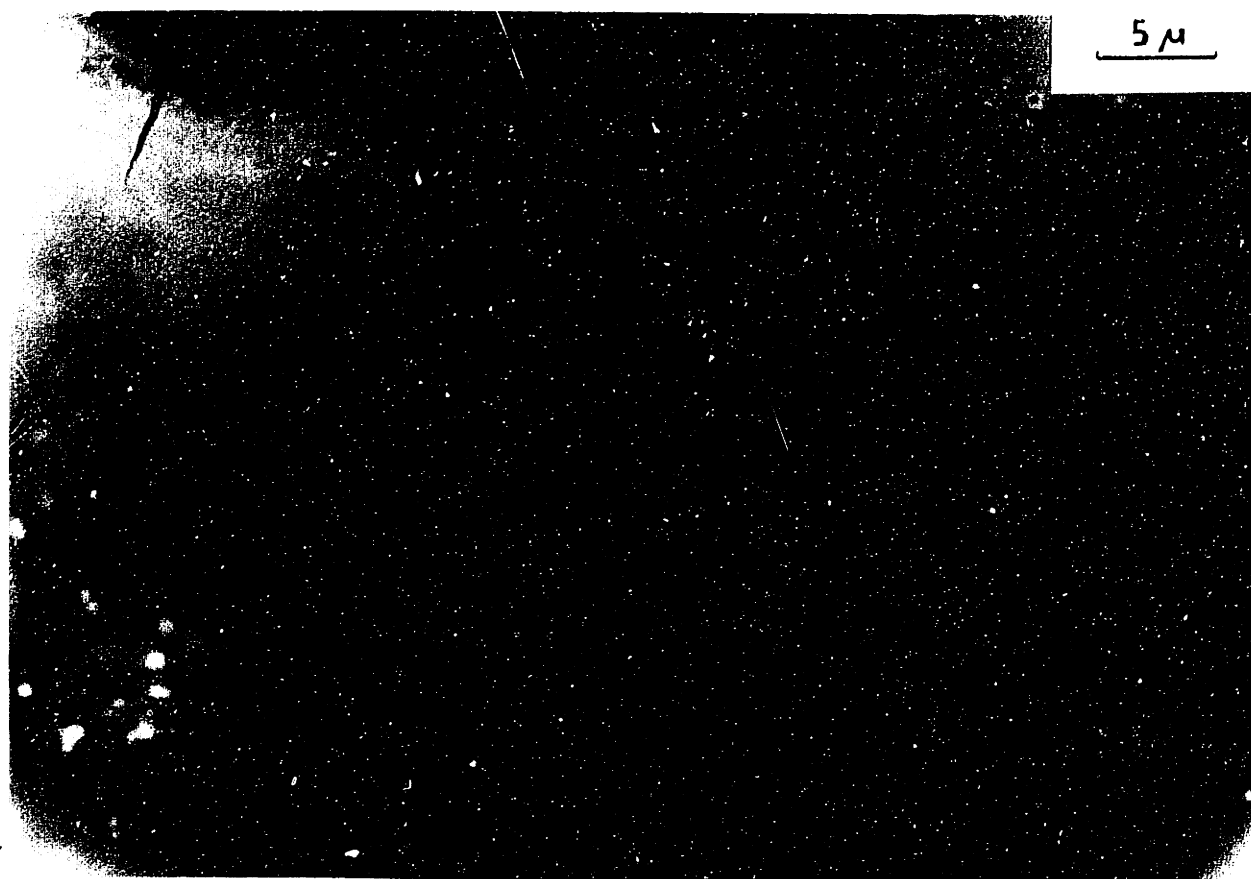
Figure 25 : Scanning transmission electron microscope (S.T.E.M.)
          image of annealed zircaloy 2.
          Low magnification annular dark field image.

counts/channel (20eV)

1024

Zr (L)

Fe (K$_\alpha$)

Ni (K$_\alpha$)

(K$_\beta$)

(K$_\beta$)

Zr (K$_\alpha$)

(K$_\beta$)

2.04   6.39 7.46   15.70   Energy keV
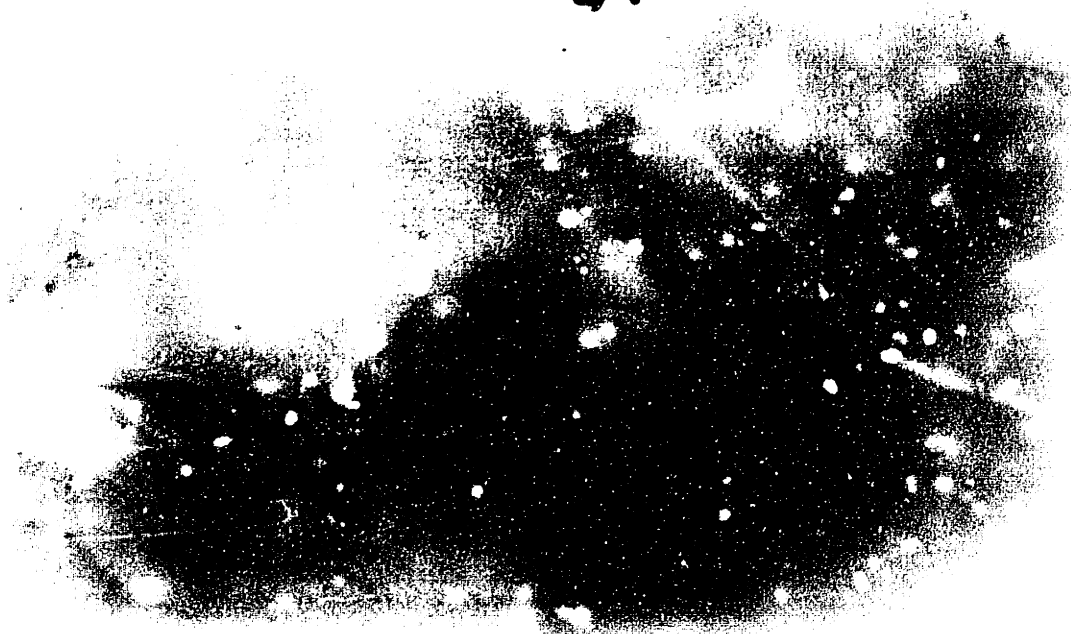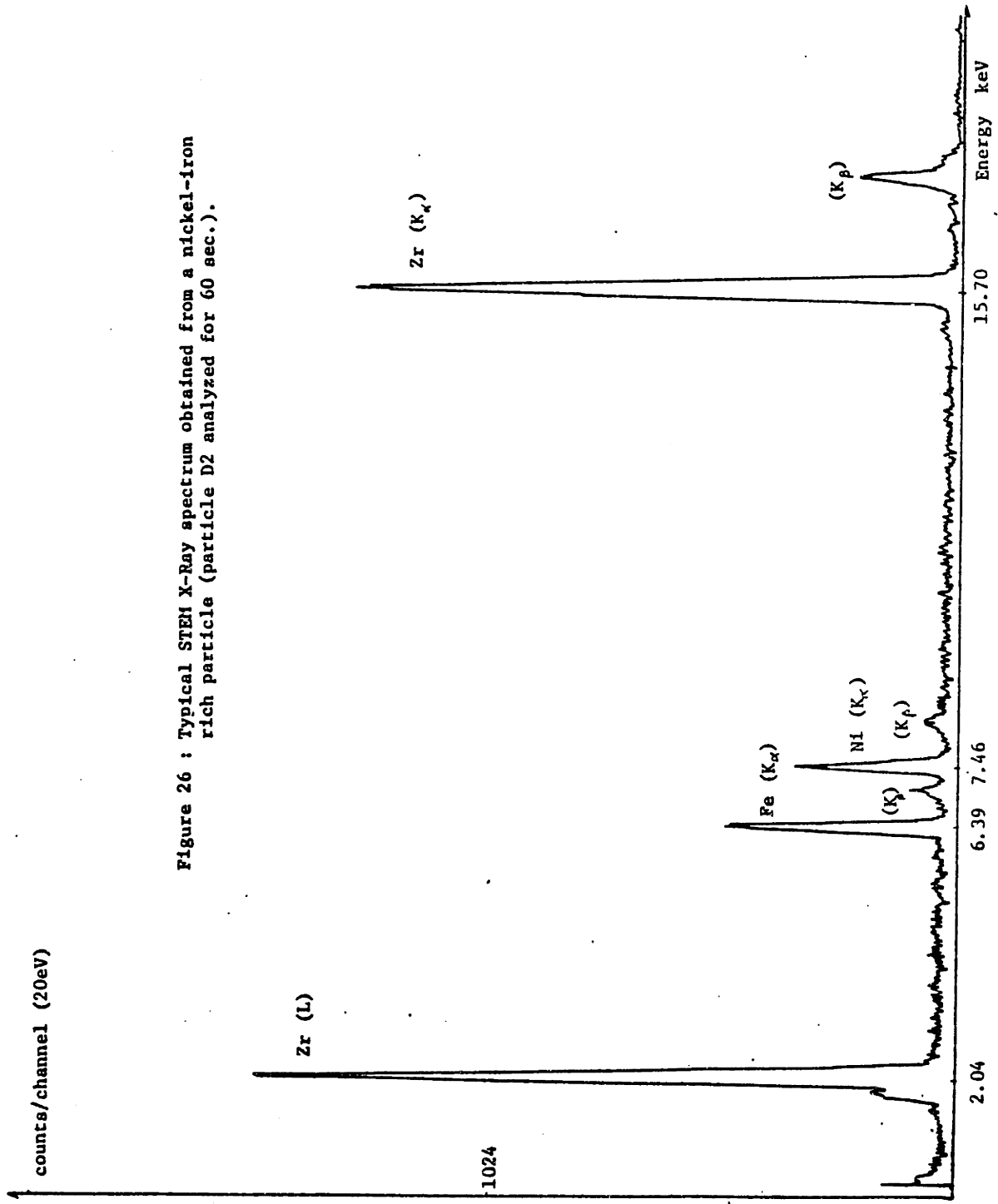
Figure 26 : Typical STEM X-Ray spectrum obtained from a nickel-iron
rich particle (particle D2 analyzed for 60 sec.).
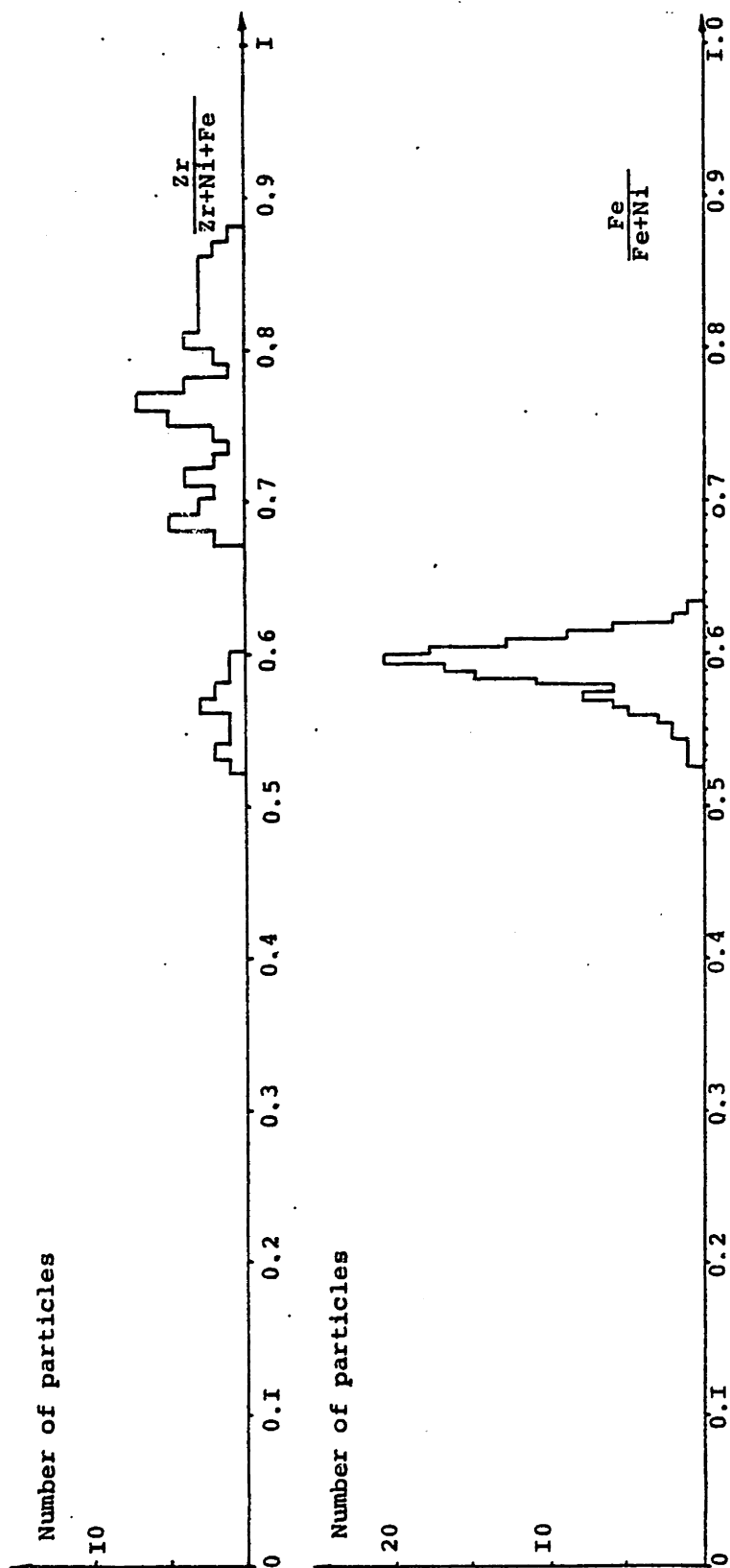
Figure 27 : Statistical distribution of the nickel-iron rich particles analyzed in situ.
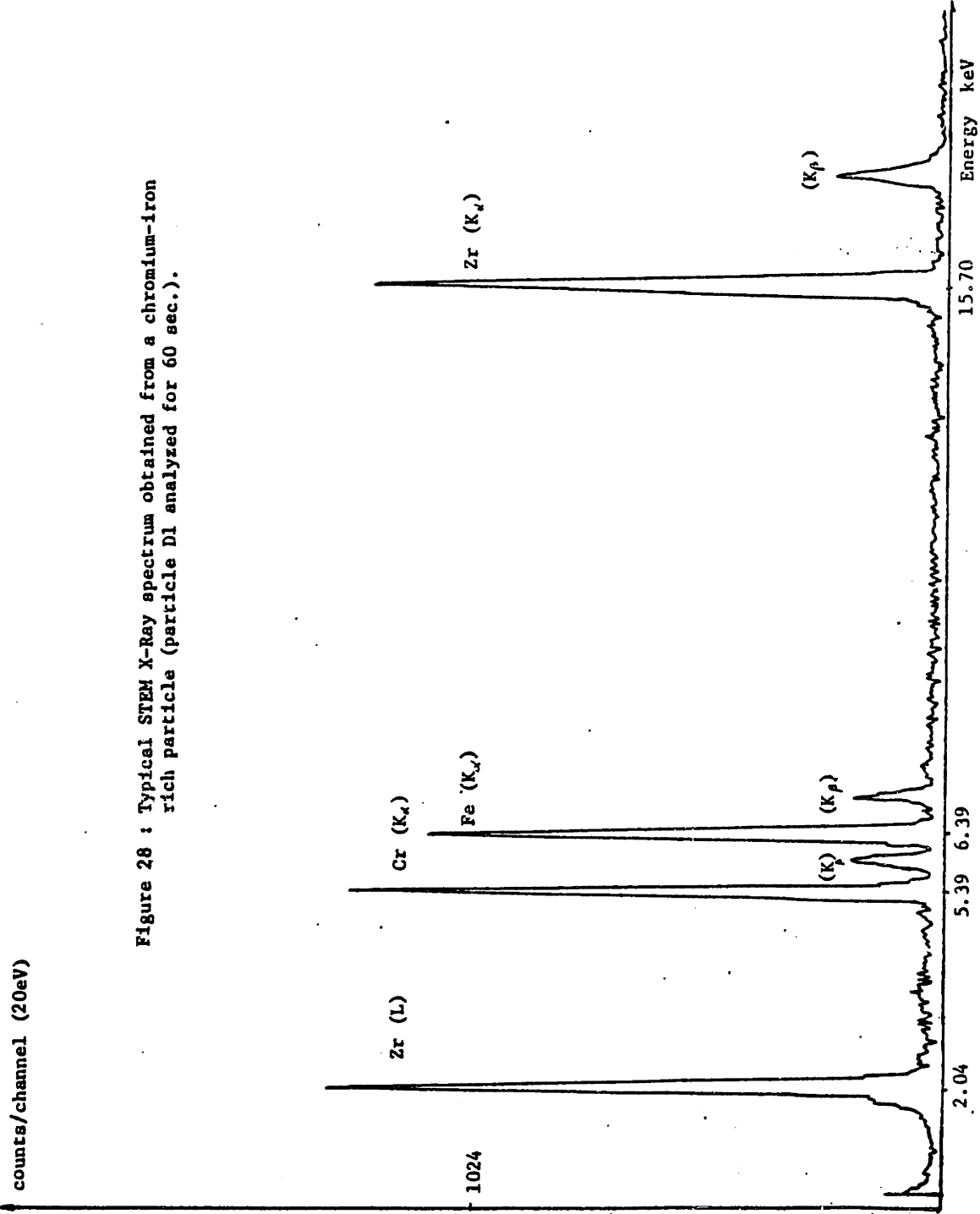
Figure 28 : Typical STEM X-Ray spectrum obtained from a chromium-iron rich particle (particle D1 analyzed for 60 sec.).
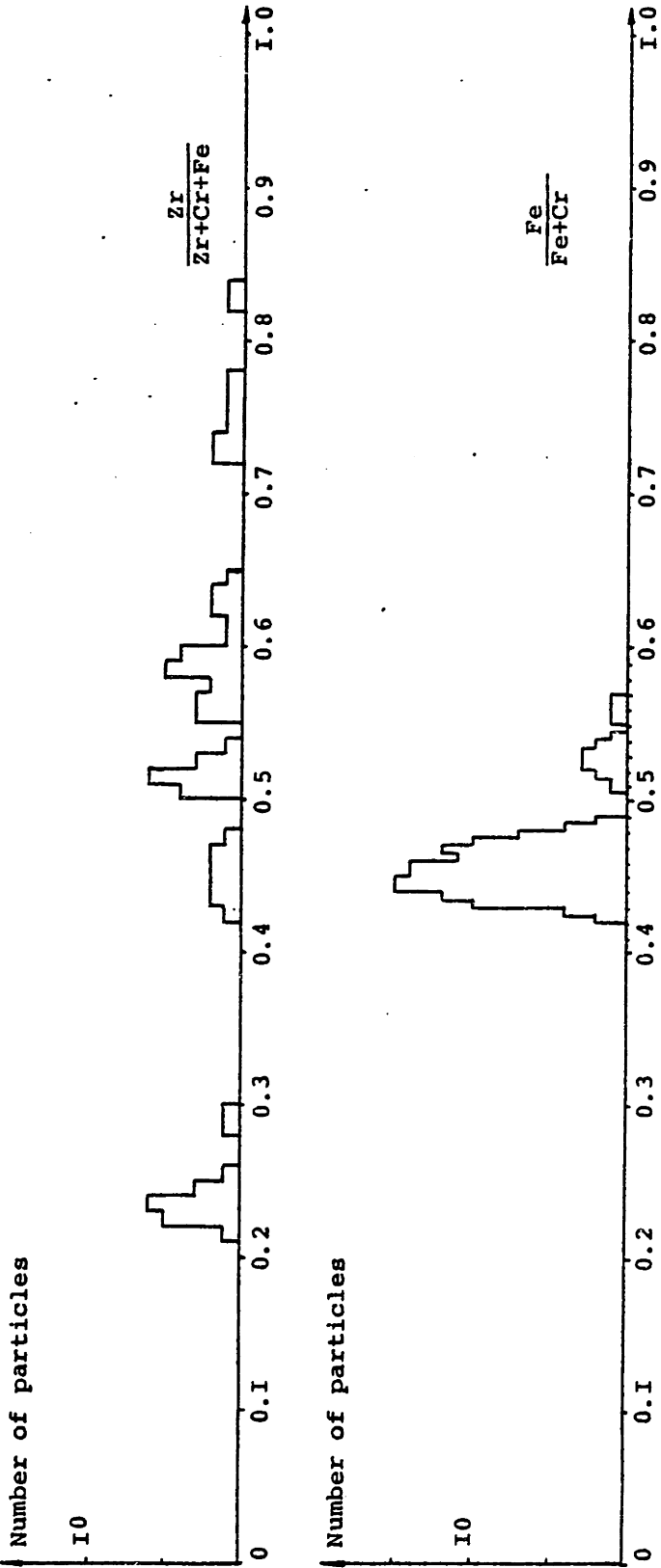
Figure 29 : Statistical distribution of the chromium-iron rich particles analized in situ.
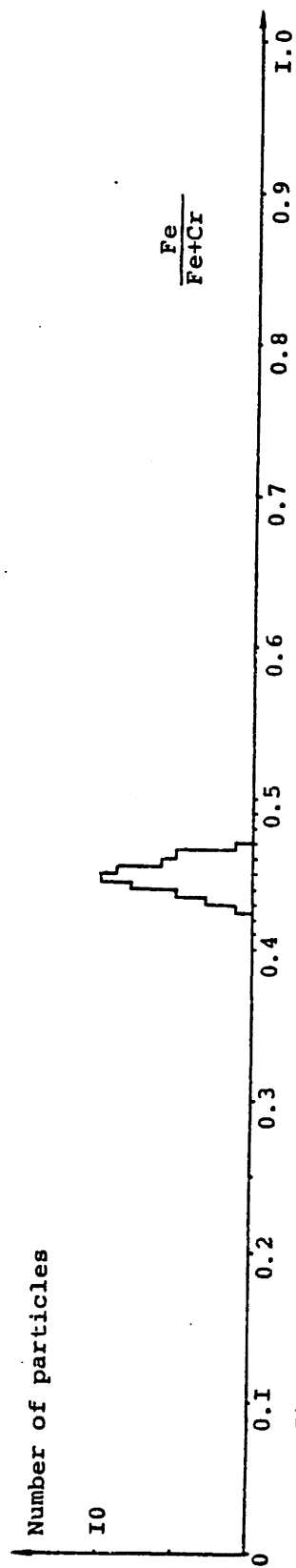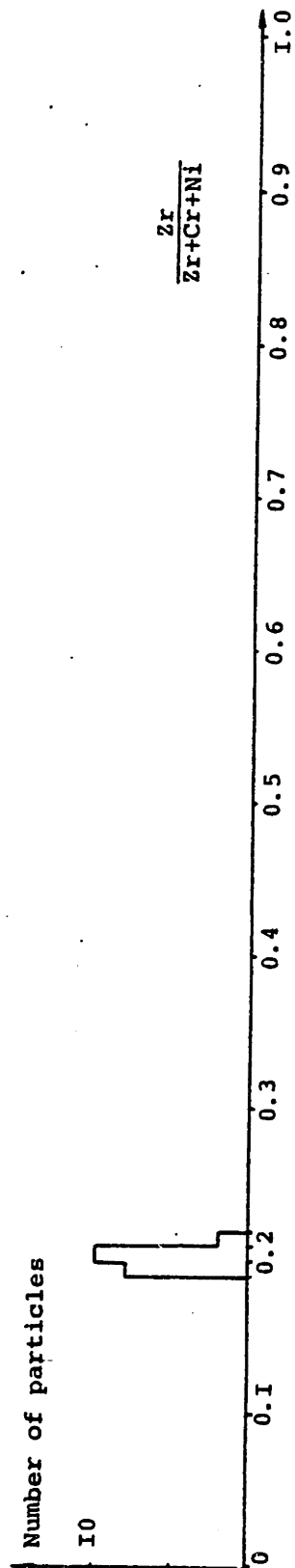
Figure 30 : Statistical distribution of the chromium-iron rich particles analyzed on extraction replicas.
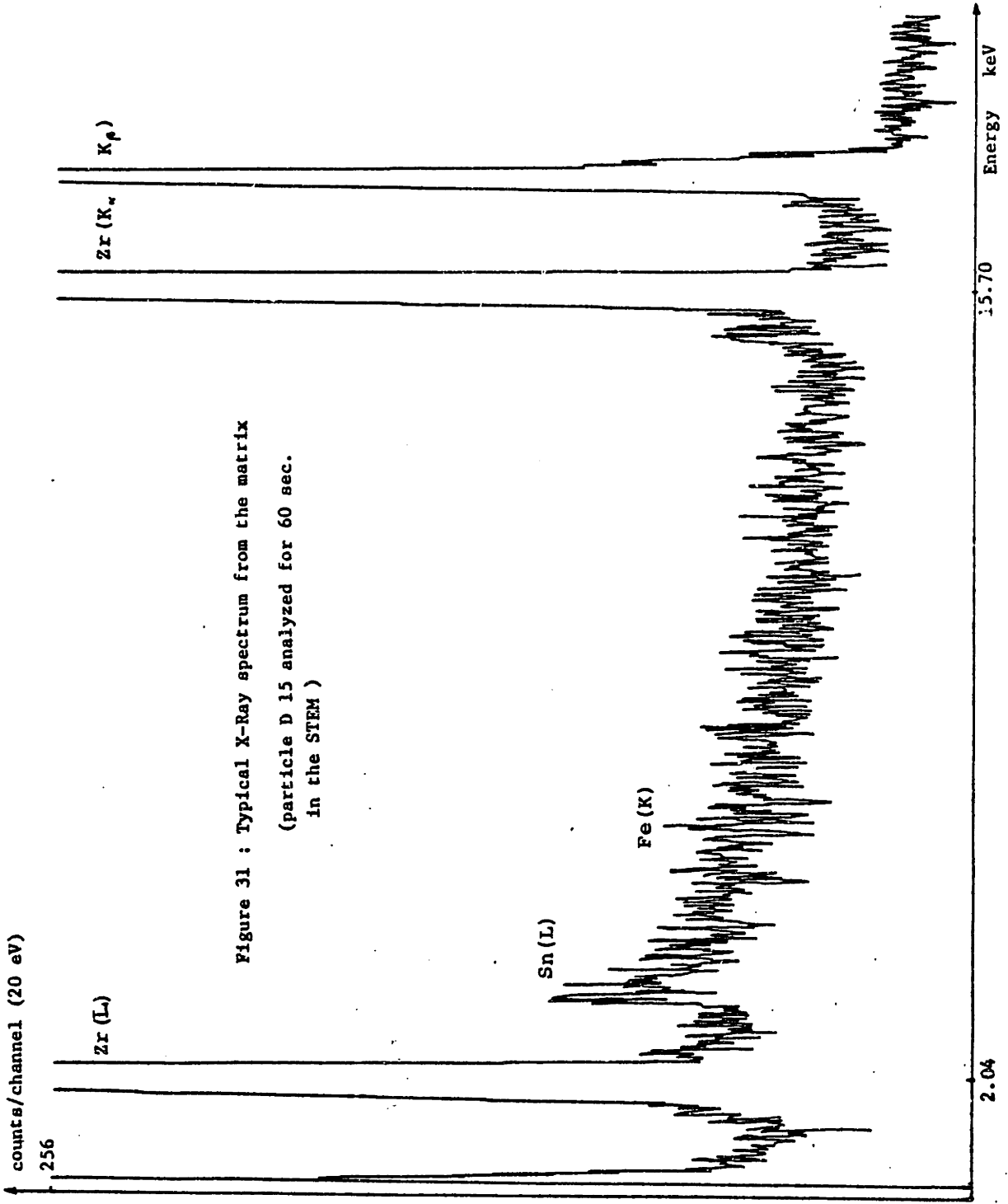
Figure 31 : Typical X-Ray spectrum from the matrix

(particle D 15 analyzed for 60 sec. in the STEM)
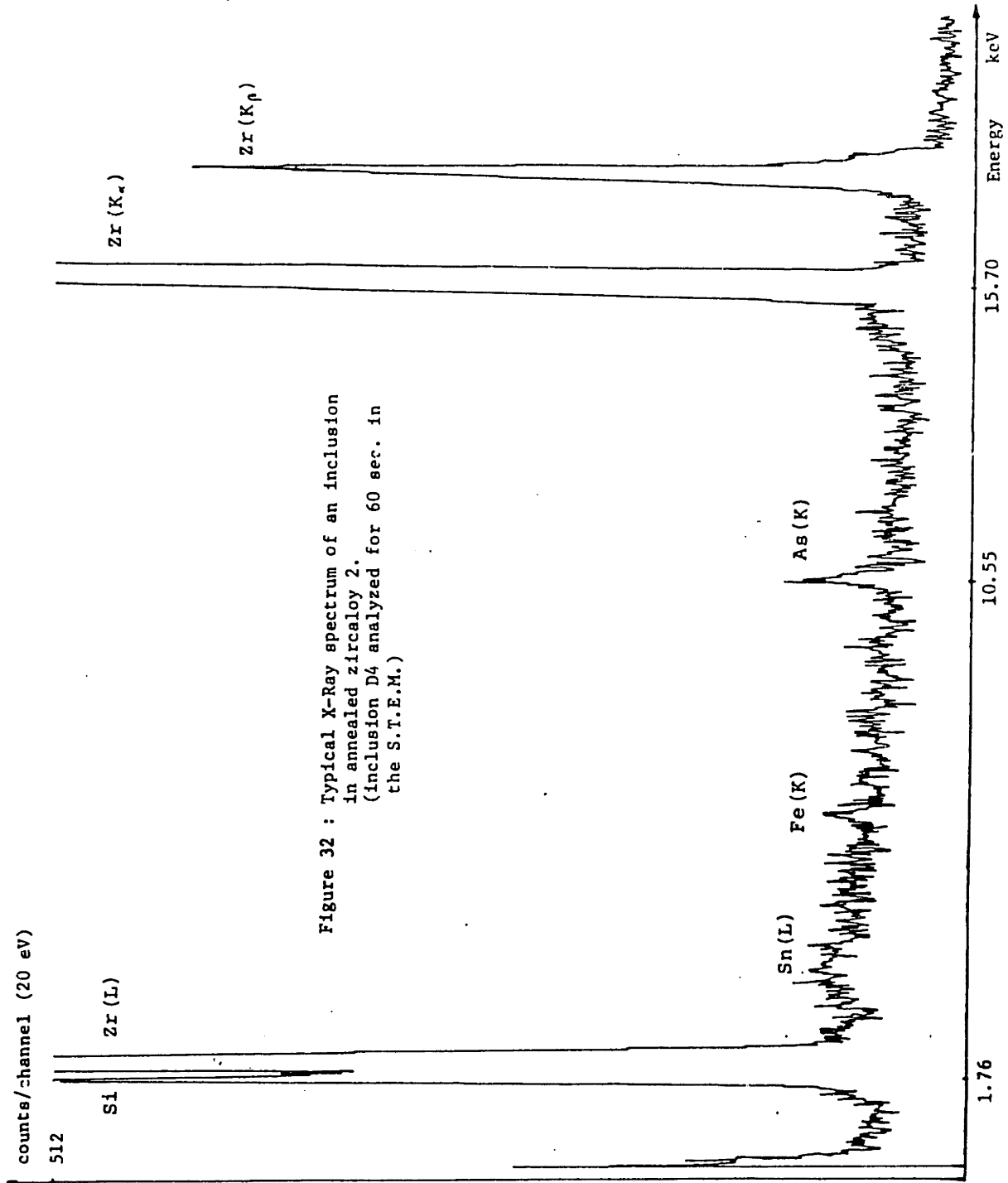
Figure 32 : Typical X-Ray spectrum of an inclusion
in annealed zircaloy 2.
(inclusion D4 analyzed for 60 sec. in
the S.T.E.M.)

analyzed intermetallic particles extracted were of the Zr-Cr-Fe type with a Fe/Cr ratio of 45/55 and a constant Zr index of 0.2 (Figure 30).

Tin was not detectable in any of the particles. However, a low signal was obtained for the energy of tin when the matrix was analyzed. A typical matrix X-Ray spectrum is given in Figure 31. There was no evidence of any segregation of tin in any analyzed compound or boundary. The inclusions described in Part IV.3d. were also analyzed and confirmed the presence of silicon suspected from electron diffraction analysis. In addition to silicon, weak peaks corresponding to tin, iron and arsenic (or lead) were observed. Such a spectrum is given in Figure 32.

V. DISCUSSION

Particle distribution

The mean spacing between particles could not be determined using the TEM because the thickness of the foil was not constant. In addition, many particles were partially or completely etched out. In the SEM, as the X-Ray analysis indicated, only chromium iron rich particles were remaining in relief above the surface of the matrix. The nickel rich particles were etched out. The fraction of pits corresponding to particles (chromium or nickel) cannot be determined and the mean number of particles per unit area could not be determined. It is likely that a particular chemical attack of the surface will etch preferentially the matrix and show the two types of particles allowing a better measurement of the particle density which is related to the volume fraction of second phase.

Clusters of Zr_2Ni and $ZrCr_2$ phases

Clusters of particles have not been described in the literature. They are present in annealed zircaloy and always exhibit the same constitution: a central nickel particle with one or two attached particles on opposite sides. Two hypotheses can be considered at first to interpret the formation of these clusters: (a) a compound containing iron, nickel and chromium, stable at higher temperature decomposes during annealing or cooling and transforms to the clusters observed. (b) The chromium iron phase nucleates on the nickel iron phase.

If the first hypothesis is correct, clusters of the unknown "mother" phase should be present in the cold worked, stress relieved material.

If the iron chromium nickel compound has a defined composition, the ratio of the volumes of each type of phase in a cluster should be constant and this has not been observed. The "reordering" of a single compound is more likely to occur on a finer scale than 0.2 μm.

There are several arguments in favor of the second hypothesis. The germinating chromium phase can grow more easily on a nickel particle (a) because some interfacial energy is available and we know by electron diffraction that the lattices of the two compounds have similarities. A simple crystallographic relationship between the nickel rich and the chromium rich particle is concluded from Figure 20 to be:

$$(1\bar{1}0)_{Zr_2Ni} \; // \; (10\bar{1}1)_{ZrCr_2}; \quad (002)_{Zr_2Ni} \; // \; (\bar{2}110)_{ZrCr_2}$$
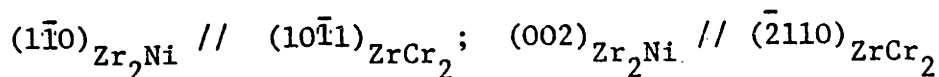
(b) because the chromium rich particles contain little nickel and there is a depletion of the nickel content of the matrix near the particle-matrix interface. One should note however that the maximum solubility of nickel in the chromium rich particles and in the matrix are not known and that there is also a depletion of iron near the interface.

This heterogeneous nucleation would indicate that the nickel rich particles are precipitated first. This cannot be concluded from the binary systems (which give temperatures of 845°C and 835°C for the precipitation of Zr_2Ni and $ZrCr_2$ respectively), because iron is present in large amount in the identified phases.

Crystallographic structure of the particles

The crystallographic structures of the two types of intermetallics are very close to the structure of Zr_2Ni and $ZrCr_2$. Within the accuracy of the measurements (1%) the lattice spacings of Zr_2Ni and $ZrCr_2$ can be

used to index the diffraction patterns. Several electron diffraction

images of $ZrCr_2$ are very close to the patterns of Zr_2Ni. e.g. $(111)_{Zr_2Ni}$

and $(1\bar{2}13)_{ZrCr_2}$ or $(001)_{Zr_2Ni}$ and $(1\bar{2}10)_{ZrCr_2}$. In general several

patterns of the same particle are necessary to identify it as chromium

rich or nickel rich (unless patterns such as $(0001)_{ZrCr_2}$ or (001) are

obtained). The $ZrCr_2$ type compound shows a band structure that has

been described as a f.c.c.- h.c.p. packing by Versaci and Ipohorski (26)

with $[110]_{fcc}$ parallel to $[1210]_{hcp}$ and $[111]_{fcc}$ parallel to $[0001]_{hcp}$.

No diffraction pattern corresponding to the cubic structure has been

obtained. The platelet structure of the particle was responsible for

streaks in the [0001] direction. As $ZrCr_2$ has a hexagonal structure, it

is likely that the platelets are twins or stacking faults. These

were present only on large precipitates and could be produced by

deformation on cooling.

A second possible explanation is the formation of hexagonal $ZrCr_2$

from fcc $ZrCr_2$ but there is no evidence of presence of fcc $ZrCr_2$ in

zircaloy 2. Some electron diffraction images corresponding to high

index poles showed variations in intensity related to variations of

structure factor. The structure factor has not been calculated for the

different reflections of $ZrCr_2$ or Zr_2Ni but since Fe and Ni and Cr have

close atomic scattering factors, because their atomic mass is similar,

while the Zr atom is much heavier, it is likely that such variations in

spot intensity are present in $ZrCr_2$ and Zr_2Ni. For both intermetallic

particles, in particular electron diffraction patterns, additional spots

were observed, corresponding to ordering of the structure on a larger

scale than the $ZrCr_2$ or Zr_2Ni structure. Vitikainen (23) reports the

(3.89A)
10Ī1

74°

0000

(4.23A)   (2.12A)

1Ž12
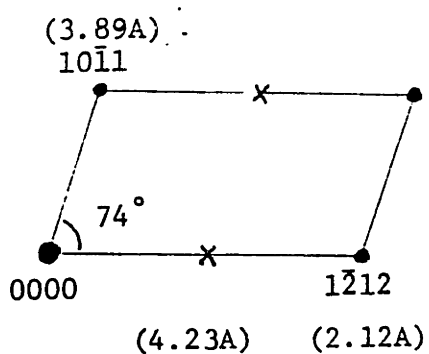
(Ŝ416)   ZrCr$_2$ type

x: additional spot

002
(2.70A)

000   1Ī0
(4.58A)
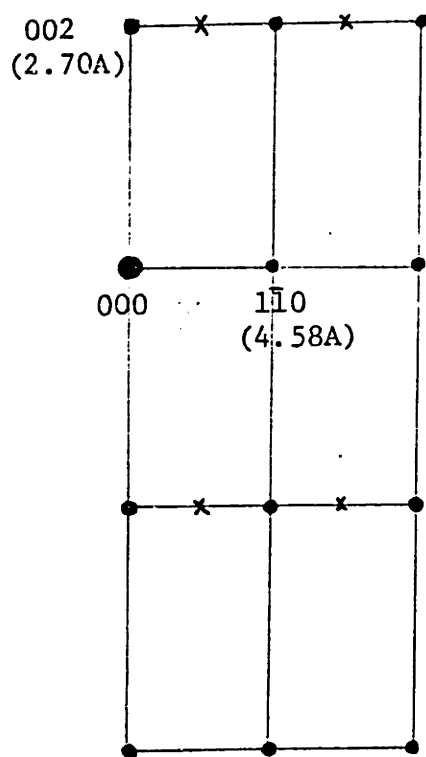
(110) Zr$_2$Ni type

x: additional spot

streak

31Ī0
(1.22A)

0000   0002
(4.14A)
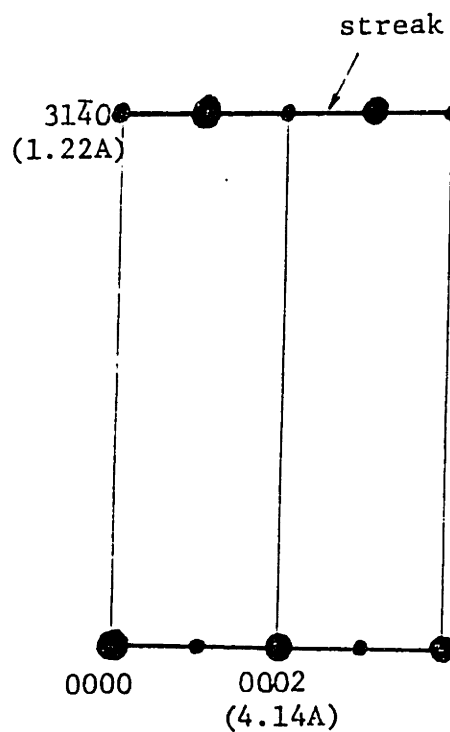
(Ŝ520) ZrCr$_2$ type

● strong spot
● weak spot

Figure 33 : Electron diffraction patterns of the intermetallic
particles presenting surstructure reflexions and
stucture factor influence.

(101) reflection as missing in the (010) pole but visible in the (111) pole. Examples of these two phenomena are given in Figure 33.

Chemical Composition of the Particles

According to the electron diffraction data, the structure of the two compounds is very close to $ZrCr_2$ and Zr_2Ni so that it is probable that iron is substituting for Cr or Ni, respectively. The sizes of Cr, Ni and Fe atoms are comparable. However, Cr could not be detected in the Zr_2Ni type of particles, neither could Ni be found in the $ZrCr_2$ type. As it was shown by the statistics on the composition of particles (Figures 27, 29 and 30), if there is substitution, the amount of element substituted is constant for each type of particle. It can be dependent on heat treatment. Zircaloy 2 contains 0.05 wt% Ni, 0.1 wt% Cr and 0.15 wt% Fe. The atomic mass of Fe, Ni and Cr are close and the concentrations verify $[Cr] = 2[Ni]$ and $[Fe] = [Cr] + [Ni]$. In the $ZrCr_2$ type of particles $[Cr] = [Fe]$ and in the Zr_2Ni type $[Ni] = [Fe]$ as a first approximation. As the solubility of Ni and Cr is very small in α zirconium, one can expect a precipitation of phases depleting nearly completely the matrix in Fe, Ni and Cr. If the particles are well defined compounds, one can expect other phases containing Fe, Ni or Cr to precipitate after long annealing times in most cases. As it has been shown recently by J.M. Grange (31) in zircaloy 4 the formation of iron rich phases (dzeta and Zr_4Fe) can occur with adequate heat treatments.

Previous investigators found it difficult to determine the chemical composition of particles in zircaloy 2 because they are of submicron size and a conventional microprobe with a volume resolution of 1 μm^3 is not accurate enough. Östberg (22) averaged the particles and analyzed only

particles larger than 1μm. Vitikainen (23) using a Jeol 200 kV, TEM with scanning ability did not obtain accurate results.

A dedicated STEM provides a strong X-Ray signal from very small volumes. To be quantitative, the STEM needs to be calibrated with known compounds and such standards were not available for this work. If the intensity of the X-Ray signal was consistent with the number of atoms of the considered chemical element, a Zr index of 0.33 for the $ZrCr_2$ type and of 0.67 for the Zr_2Ni type should be expected. The result of the $ZrCr_2$ type of particles extracted on carbon replica is 0.2. The low values of the Zr index for the Zr_2Ni type are around 0.55. When a particle is analyzed in situ, part of the signal comes from the matrix and the Zr index presents a large scatter band. Experimental and theoretical results of Zr indices are in good agreement. The smaller experimental value of the Zr index results probably from the fluorescence of the K X-Ray energy level of Fe, Cr and Ni by the high energy X-Rays of zirconium (15.4 keV) and also from a peak shape difference, the window width being 270 eV for all the elements. The Ni and Fe peaks in the Zr_2Ni type and the Cr and Fe peaks in the $ZrCr_2$ type of particles are of comparable size and of close energy. We will propose a chemical composition of $Zr_2Ni_{0.4}Fe_{0.6}$ for the Zr_2Ni type of particles and $ZrCr_{1.1}Fe_{0.9}$ for the $ZrCr_2$ type of particles. This result is quite different from the analysis of Vander Sande and Bement (15) of the $ZrCr_2$ type of particles in zircaloy 4 where a $Zr_xFe_5Cr_2$ composition is suggested.

Tin in Zircaloy 2

According to the phase diagrams, in the binary alloy zirconium 1.5 wt% tin, precipitation occurs below a temperature close to 500°C.

However, at temperatures below 500°C, the kinetics of precipitation

can be very slow. In the annealed and in the cold worked stress relieved

zircaloy 2 considered here, tin could be detected only in the matrix.

There was no concentration of tin in other intermetallic particles or at

interfaces. If tin rich particles were present, they were not observed in

bright field. If they are small enough to be confused with the graininess

of the image due to oxidation, they are probably coherent with the matrix

and might give rise to additional spots in electron diffraction. We did

not find these features and we will conclude that tin is in solid solution

in the as received material.

Inclusions

Only one kind of inclusion was observed in zircaloy 2. The electron

diffraction as well as the chemical analysis led to the identification

of the Zr_3Si type of silicide. Some diffraction patterns are given in

Appendix C. The chemical analysis in the STEM showed the presence of

other elements in these inclusions. For example, lead or arsenic. The

distinction between lead and arsenic could not be made because the

signal is weak and mainly one line is observed. The energy resolution

and the accuracy of calibration of the energy dispersive X-Ray analyser

were insufficient. The arsenic content of zircaloy 2 is not usually

determinated. No recorded compound fitted all these data. No carbide

or other inclusion than the ones containing silicon were observed.

Zirconium carbides of ZrC type can be easily identified in electron

diffraction as they are of cubic structure with $a_o = 4.7 \text{Å}$.

VI. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

Conclusions:

Zircaloy 2 in the annealed and in the cold worked, stress relieved condition was studied by SEM, TEM and STEM. The structures and the chemical composition of the different second phase particles were determined by electron diffraction in the TEM and by energy dispersive X-Ray microanalysis in the STEM. The alloying elements were found to be partitioned as follows:

1. Nickel is present in a tetragonal phase with a_o=6.5 $\overset{o}{A}$, c_o=5.3 $\overset{o}{A}$ similar to Zr_2Ni containing iron in partial substitution for nickel. The composition of this phase is $Zr_2Ni_{0.4}Fe_{0.6}$.

2. Chromium is present in a hexagonal phase with a_o=5.1 $\overset{o}{A}$ c_o=8.3 $\overset{o}{A}$, similar to $ZrCr_2$, containing iron in partial substitution for chromium. The chemical composition of this phase is $ZrCr_{1.1}Fe_{0.9}$.

3. Iron is partitioned in the two phases described above and very little remains in solid solution in the matrix.

4. Tin is in solid solution in the textured hexagonal matrix of α zirconium.

These intermetallic phases are uniformly distributed within the matrix with an average size of 0.3 μm. In TEM and STEM, individual precipitates as well as heterogeneous clusters of 2 to 5 particles were observed. The second phase particles were also studied with the SEM after chemical etching. The nickel rich particles were etched out. Large inclusions (1 μm) having the structure of Zr_3Si were identified.

In the cold worked, stress relieved condition, the material is partially recrystallized with elongated grains and a dense network of dislocations.

<u>Suggestion for further work</u>:

The following topics are suggested for further work:

1. Determination of the volume fraction and mean interparticle spacing in the annealed condition.

2. Quantification of the STEM X-Ray energy dispersive analysis results with Cr-Ni-Fe-Zr standards.

3. Analysis of the size and distribution of second phase particles in the cold worked, stress relieved material.

4. Analysis of the microstructure after β processing.

5. Investigation of further precipitation and cavitation after creep deformation.

6. Correlation between corrosion rate and corrosion initiation sites and second phase particles.

7. Stability of the solid solution of tin.

APPENDIX A

CRYSTALLOGRAPHY OF HEXAGONAL MATERIALS

The crystallography of hexagonal close packed metals has been reviewed recently by P.G. Partridge (32). It is not the aim of this appendix to describe the hexagonal lattice but the reader will find here some tables and basic information that were useful for the present study.

The most important directions and planes are given in Figure A1. The four Miller-Bravais index notation has been used. This notation conserves a similarity between equivalent directions or planes and is used in the stereographic projection. The reader not familiar with the stereographic projection is referred to Cullity (33). For hexagonal materials, on a (0001) standard projection, the position of the poles corresponding to pyramidal planes depends on the c/a ratio of the material. For precise work, a stereographic projection corresponding to the specific material of interest is necessary. The angles between the most important planes are given for zirconium in Table A1.

In order to facilitate one's construction of poles in the stereographic projection as well as to find a pole quickly, the following set of coordinates are proposed: As $h+k+i=0$, (hkil) being the Miller-Bravais indices, two integers among $\{h,k,i\}$ are of the same sign. (Zero can be considered as positive or negative indifferently.) In the following, we will consider h and k both positive as an example. We will choose the smaller of h/k and k/h as a first coordinate x. (For instance, x=h/k if h<k). This coordinate is always between 0 and 1. The choice of these two indices indicates in which 1/12th of the standard (0001) stereographic projection the pole of indices (hkil) lies. To know how far from (0001)
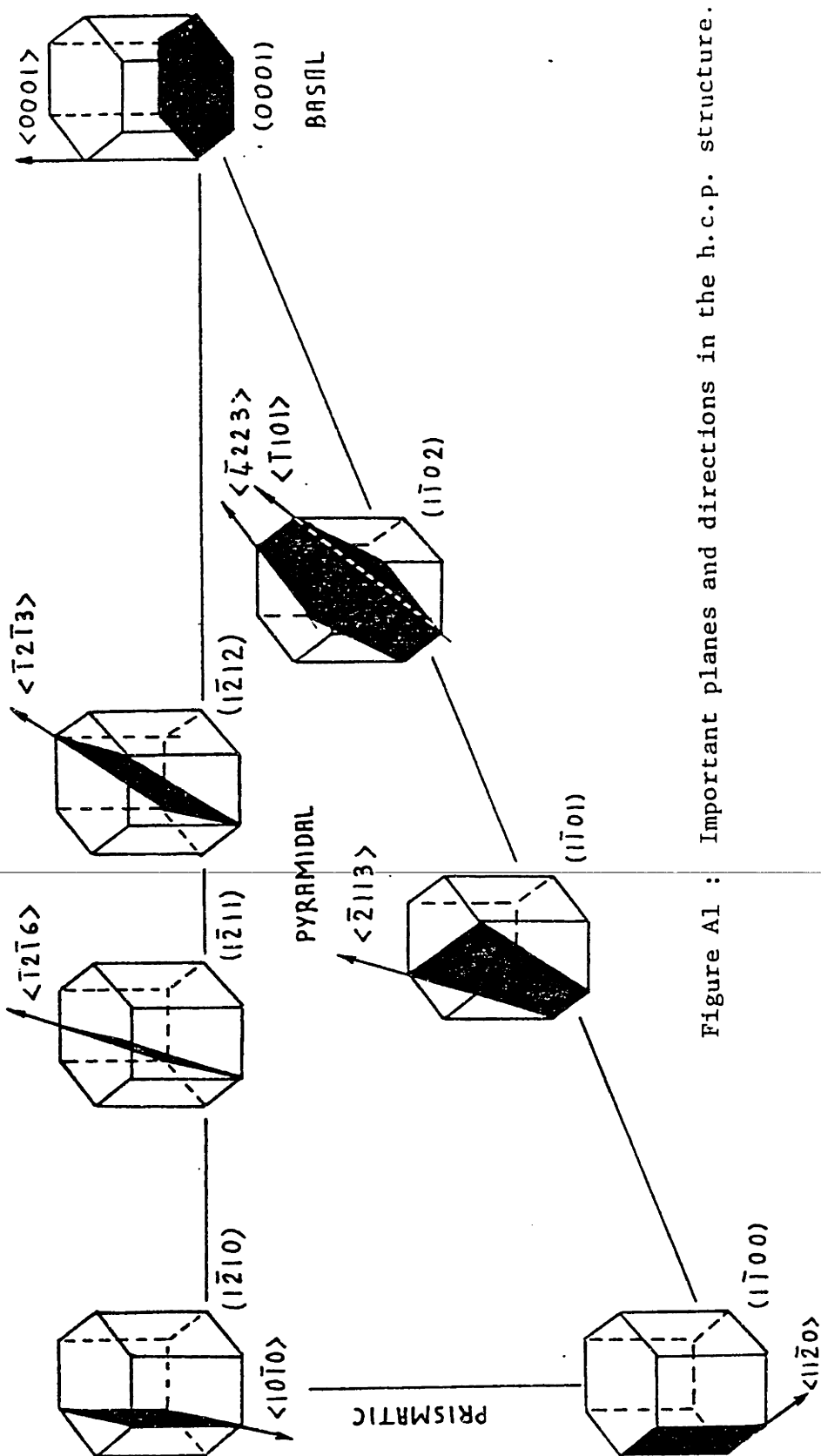
Figure A1 : Important planes and directions in the h.c.p. structure.

hkil \ hkil'	1̄210	01̄10	0001	1̄213	2̄423	01̄11	1̄216	1̄211	01̄12	1̄543	2̄753	1̄219
1̄210	0	30	90	43.3	25.2	40.5	62.0	17.4	54.1	27.1	20.1	70.5
01̄10		0	90	50.9	38.4	28.5	66.0	34.3	47.4	22.3	21.6	73.2
0001			0	46.7	64.8	61.5	28.0	72.6	42.6	70.4	75.4	19.5
1̄213				0	18.1	28.2	18.8	25.9	21.3	28.6	31.0	27.2
2̄423					0	26.9	36.8	7.8	32.4	18.5	16.8	45.3
01̄11						0	38.9	29.7	18.9	13.4	20.4	45.2
1̄216							0	44.6	22.3	4.1	48.4	8.5
1̄211								0	38.8	18.2	13.6	53.1
01̄12									0	29.2	35.4	27.2
1̄543										0	7.0	52.2
2̄753											0	56.5

Table A1 :

Angles between $(hkil)$ and $(h'k'i'l')$ planes in hexagonal Zr

$$\cos\left((hkil),(h'k'i'l')\right) = \frac{hh' + kk' + \frac{1}{2}(hk' + kh') + \frac{3}{4}\frac{a^2}{c^2} ll'}{\sqrt{h^2 + k^2 + hk + \frac{3}{4}\frac{a^2}{c^2} l^2}\ \sqrt{h'^2 + k'^2 + h'k' + \frac{3}{4}\frac{a^2}{c^2} l'^2}}$$

with $c/a = 1.593$

the (hkil) plane is, one needs a second coordinate and we will choose

$y = 1/u$ where u is the third index remaining after the choice of the two

others to define x. In our example $y = 1/i$.

Figure A2 shows the standard (0001) stereographic projection for Zr_α.

The sign of the different indices as well as the net of coorrinates

(x,y) for zirconium are indicated. The data to construct such a net

is given in Figure A3 and Table A2.
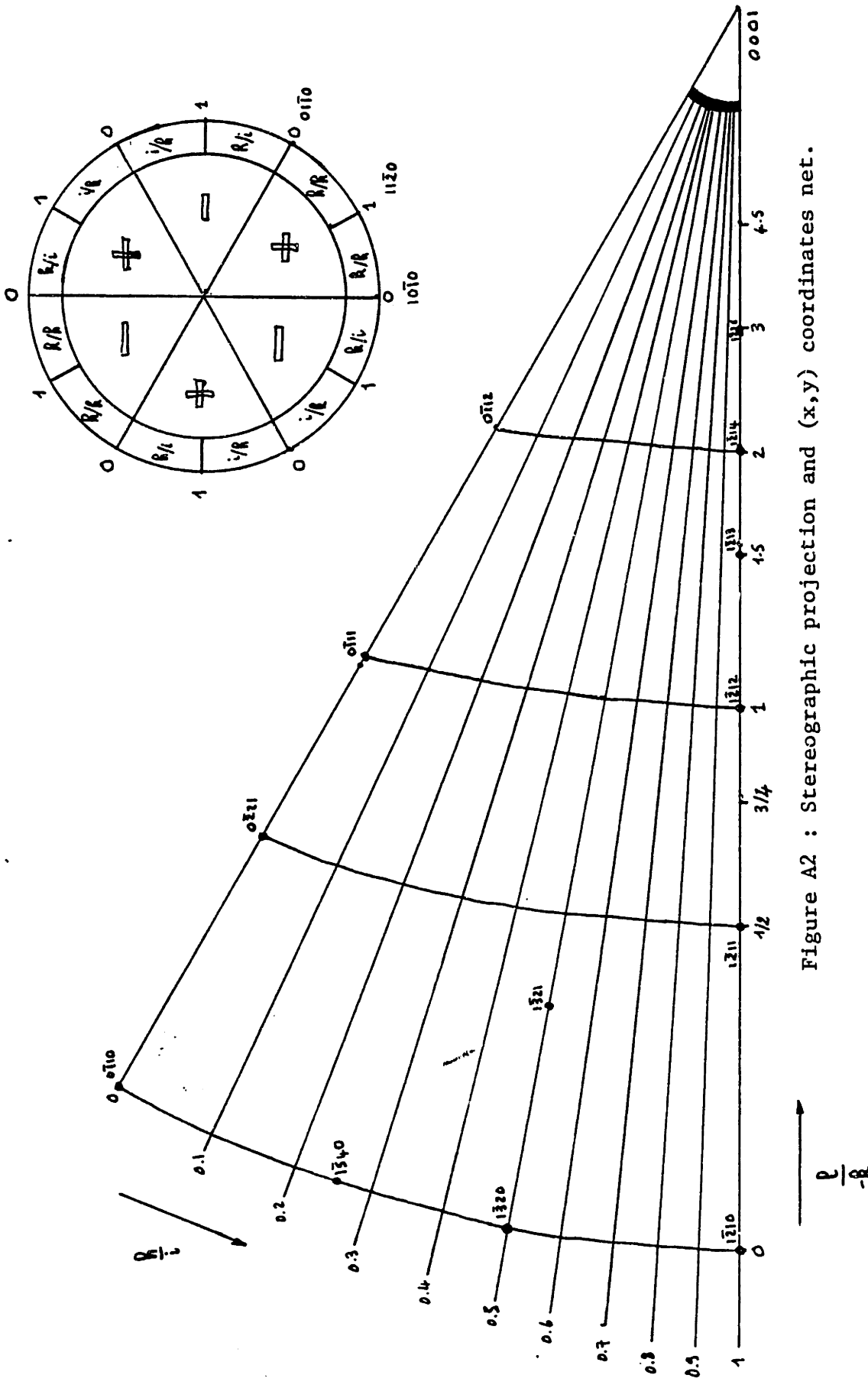
Figure A2 : Stereographic projection and (x,y) coordinates net.

Figure A3 : Definition of the (x,y) coordinates system.
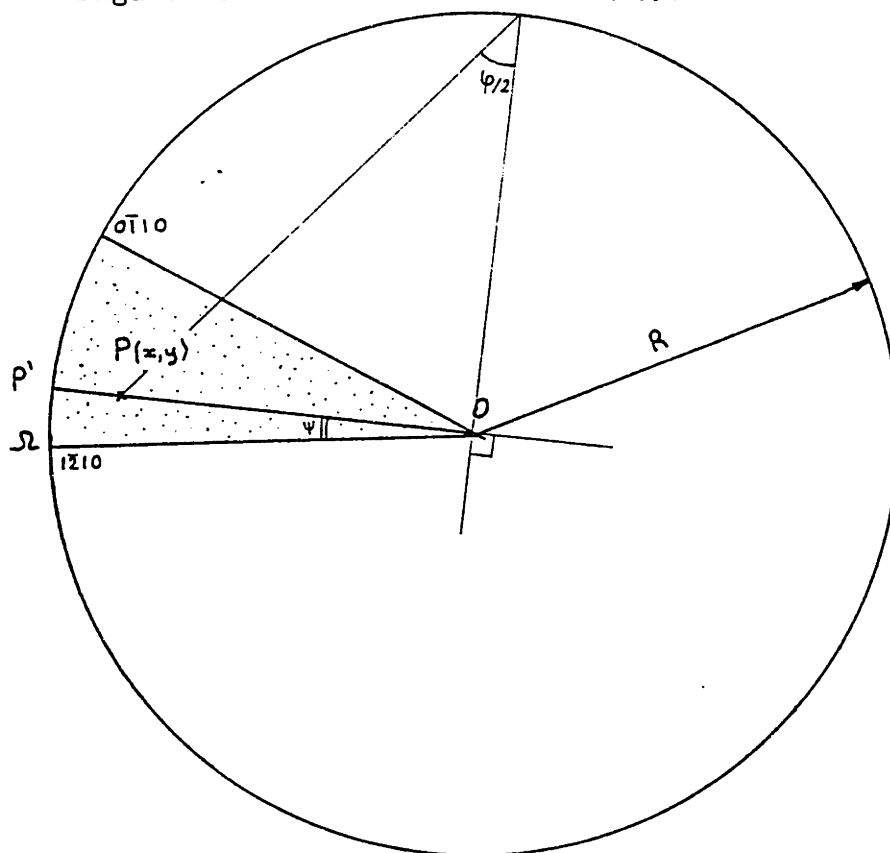
P is defined by the coordinates (x,y) or by the Miller indices $h\,k\,i\,\ell$

In the case of the drawing $h>0$ $k<0$ $i>0$ $\ell>0$

$$h \leq i$$

$$x = \frac{h}{i} \qquad y = -\frac{\ell}{k}$$

$\widehat{OP} = \varphi$ and the length of OP is $R\,tg(\varphi/2)$

$$\cos \psi = \frac{1}{\beta}$$

$$tg\,\varphi = \frac{c}{a}\,\frac{\beta}{y}$$

with $\beta = \frac{2}{\sqrt{3}}\,\dfrac{\sqrt{1+x+x^2}}{1+x}$

and $\dfrac{c}{a} = 1.593$ for Zr_α

Table A2 : Computed parameters for the construction of the (x,y) net
[of coordinates.

x	$\psi(x)^°$	$tg\left[\psi(x,y)/2\right]$ *				
		$y=.5$	$y=1$	$y=2$	$y=3$	$y=4$
0	30.	0.764	0.594	0.390	0.282	0.219
.1	25.3	0.756	0.582	0.378	0.272	0.210
.2	21.1	0.749	0.573	0.369	0.265	0.204
.3	17.3	0.744	0.566	0.362	0.259	0.200
.4	13.9	0.741	0.562	0.358	0.256	0.197
.5	10.9	0.738	0.558	0.354	0.253	0.195
.6	8.2	0.736	0.556	0.352	0.251	0.194
.7	5.8	0.735	0.554	0.351	0.250	0.193
.8	3.7	0.735	0.553	0.350	0.249	0.192
.9	1.7	0.734	0.553	0.350	0.249	0.192
1	0	0.734	0.553	0.349	0.249	0.192

* given for $c/a = 1.593$

y		$tg\left[\psi(x,y)/2\right]$ *	
		$x=0$	$x=1$
0.25		0.873	0.855
0.33		0.835	0.812
0.67		0.701	0.665
0.75		0.672	0.634
1.33		0.510	0.467
1.5		0.475	0.432
1.67		0.443	0.401

APPENDIX B

ELECTRON DIFFRACTION OF ZIRCALOY 2

In electron diffraction, two main features are to be considered: (a) the spot patterns and (b) the Kikuchi lines. For electron diffraction theory, the reader is referred to Hirsh (34) and for Kikuchi lines to G. Thomas (35). One should consider the spot as part of the "reciporal lattice" (Figure B1). Some reflections are not observed in high order index poles but occur usually by double diffraction in poles such as $(2\bar{1}\bar{1}0)$. Twelve of the most densely populated reciprocal lattice planes are presented in Figure B2. They can be partitioned into three categories as shown in Table B1. The repartition and the angular relationship between these 12 poles is given in Figure B3.

When the crystal is thick enough, sets of lines can often be observed superimposed on the diffraction patterns. These lines are very useful to determine precisely the direction of the electron beam with respect to the foil and the exact diffraction conditions. A band structure relating the spot patterns is often visible and characteristic of the crystal. Maps and composite pictures of this "Kikuchi network" can be found in the literature but they are very incomplete mainly in the spherical quadrangle $[(1\bar{2}13), (1\bar{2}10), (0\bar{1}110), 0\bar{1}12)]$.

It has been very useful to consider the simple network of "thin diffuse bands" to quickly identify the position of the beam on the map. The map of Figure B4 is given by Loretto (36). The more detailed partial maps of Figures B5, B6 and B7 have been drawn using the composite maps B8 and B9. They should not be used for measurments of angles since a wide spherical triangle has been developed on a plane resulting in abberations.
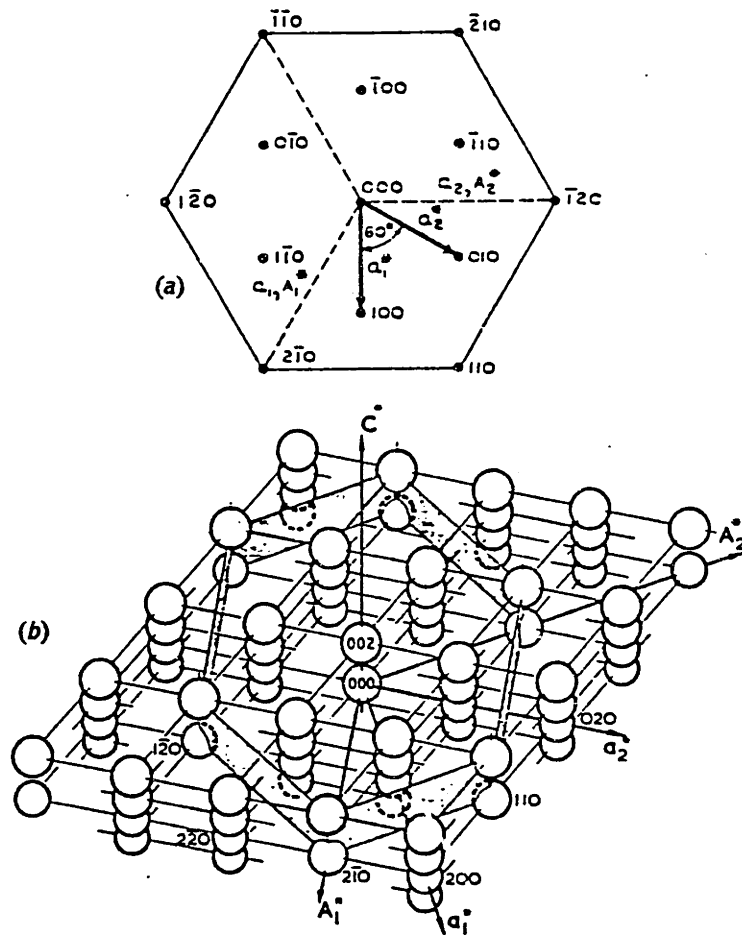
Figure B1 : Reciprocal lattice.   *a* Section parallel to (001). *b* In 3
dimensions, with lattice points omitted where ($h + 2k$) is
a multiple of 3 and *l* is odd.

a_1, a_2 direct lattice axes; a_1^*, a_2^* reciprocal latti ce axes; A_1^*, A_2^* Miller–
Bravais axes in reciprocal space.

Figure B2: Twelve of the most densely populated reciprocal lattice planes for the h.c.p. structure.

(Ī00)
(2ĪĪ0)

(02Ī)
(2Ā23)

(Ī20)
(0IĪ0)

(00Ī)
(000Ī)

(3ĪĪ)
(5Ī4̄3)

(Ī22)
(0IĪ2)

(0IĪ)
(Ī2Ī3)

(0Ī2)
(Ī2Ī6)

(4ĪĪ)
(7̄2̄53)

(Ī2Ī)
(0IĪĪ)

(03Ī)
(Ī2ĪĪ)

(0Ī3)
(Ī2Ī9)
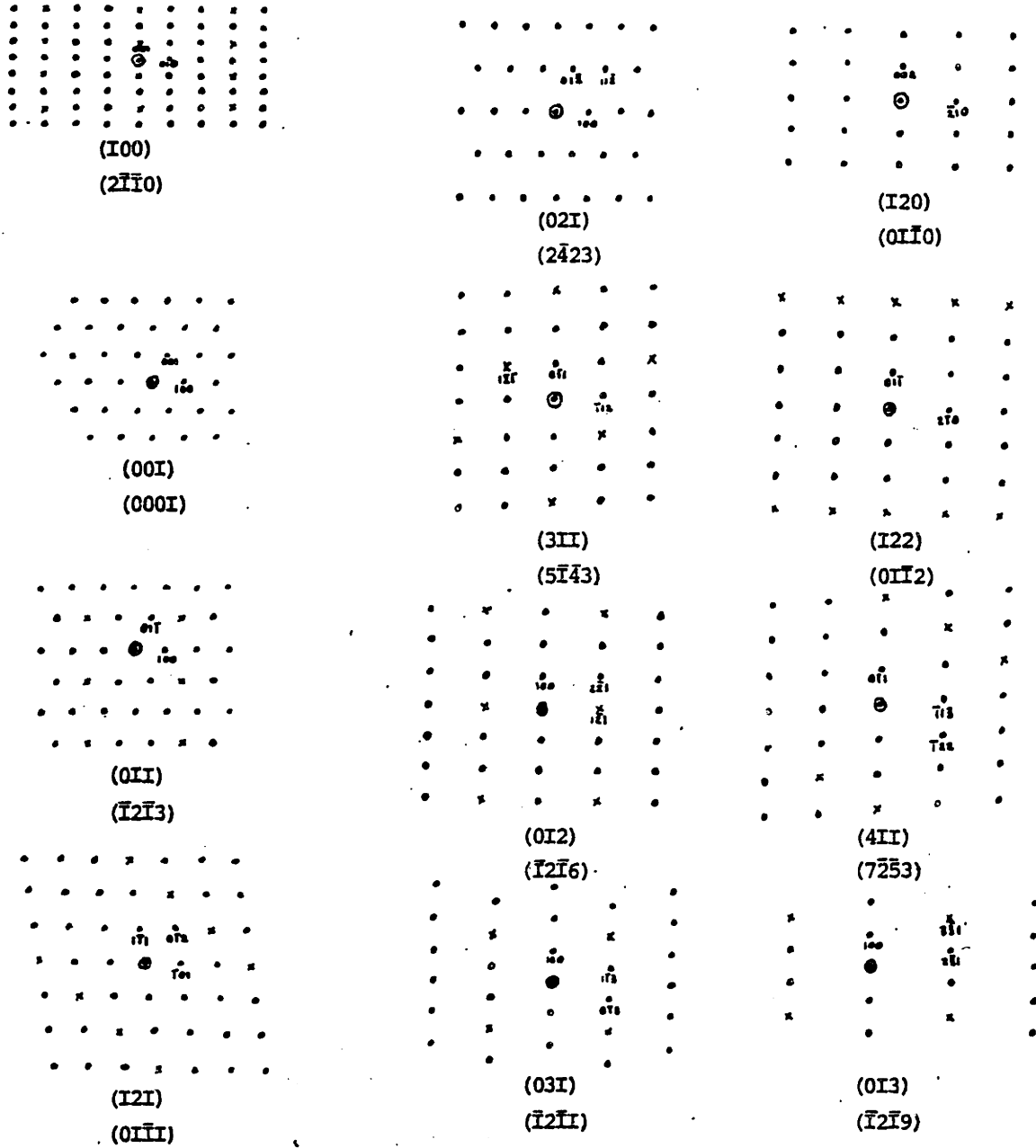
⊘ : 000   x: forbidden reflexion that can occur by double diffraction

Table B1: Twelve of the most densely populated reciprocal lattice planes for Zr_α.

a=3.232Å   c=5.147Å   c/a= 1.593

* ρ (Å⁻²)	$h_2k_2i_2l_2$ / d_2 (Å)	$h_1k_1i_1l_1$ / d_1 (Å)	φ	R_2/R_1	Type	4 indices pole	3 indices pole
14.4	$10\bar{1}0$ / 2.799	0001• / 5.147	90°	1.839	rectangle	$1\bar{2}10$	$01\bar{0}$
4.32	$\bar{1}2\bar{1}1$ / 1.542	$10\bar{1}0$ / 2.799	90°	1.815	rectangle	$1\bar{2}16$	$01\bar{2}$
4.16	$\bar{2}110$ / 1.616	0002 / 2.574	90°	1.593	rectangle	$0\bar{1}10$	$\bar{1}2\bar{0}$
3.97	$\bar{2}110$ / 1.616	$01\bar{1}1$ / 2.459	90°	1.522	rectangle	$0\bar{1}12$	$\bar{1}2\bar{2}$
9.05	$10\bar{1}0$ / 2.799	$\bar{1}100$ / 2.799	60°	1.000	X	0001	001
7.66	$01\bar{1}1$ / 2.459	$10\bar{1}0$ / 2.799	64°	1.138	X	$1\bar{2}13$	$01\bar{1}$
5.64	$01\bar{1}2$ / 1.894	$10\bar{1}0$ / 2.799	70°	1.477	X	$2\bar{4}23$	$0\bar{2}1$
4.24	$01\bar{1}3$ / 1.463	$10\bar{1}0$ / 2.799	75°	1.914	X	$1\bar{2}11$	$0\bar{3}1$
6.12	$\bar{1}01\bar{1}$ / 2.459	$\bar{1}101$ / 2.459	81°	1.000	parallelogram	$01\bar{1}1$	$\bar{1}2\bar{1}$
4.67	$\bar{1}102$ / 1.894	$10\bar{1}1$ / 2.459	87°	1.298	parallelogram	$1\bar{5}43$	$\bar{1}3\bar{1}$
3.65	$\bar{1}103$ / 1.463	$10\bar{1}1$ / 2.459	80°	1.681	parallelogram	$2\bar{7}53$	$\bar{1}4\bar{1}$
2.95	$\bar{1}3\bar{2}1$ / 1.036	$10\bar{1}0$ / 2.799	79°	2.701	parallelogram	$1\bar{2}19$	$01\bar{3}$

•: occurs by double diffraction

*: $\rho = \dfrac{d_1 \cdot d_2}{\sin\varphi}$

Figure B3 : Relation between electron diffraction patterns and (0001) stereographic projection.

Figure B4:General Kikuchi maps for c.p.h.crystals
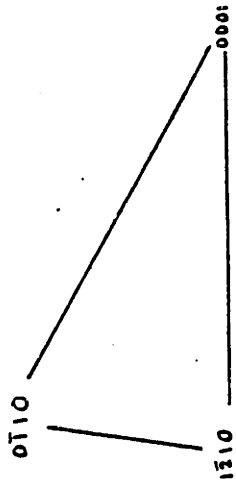
thin diffuse band
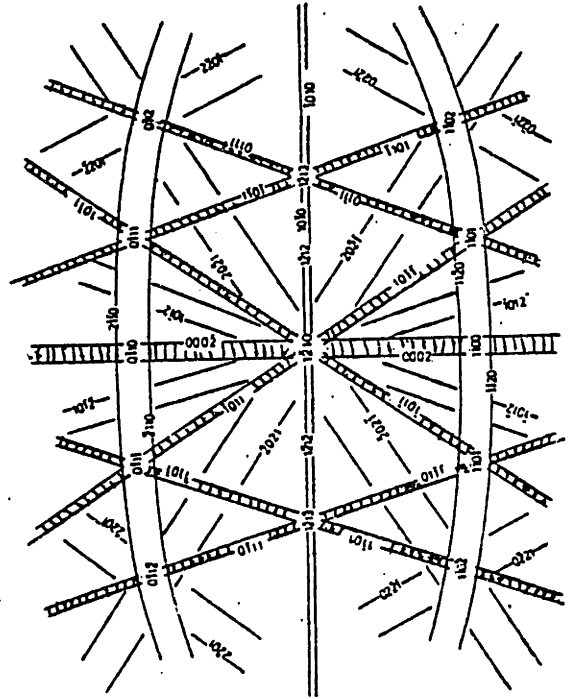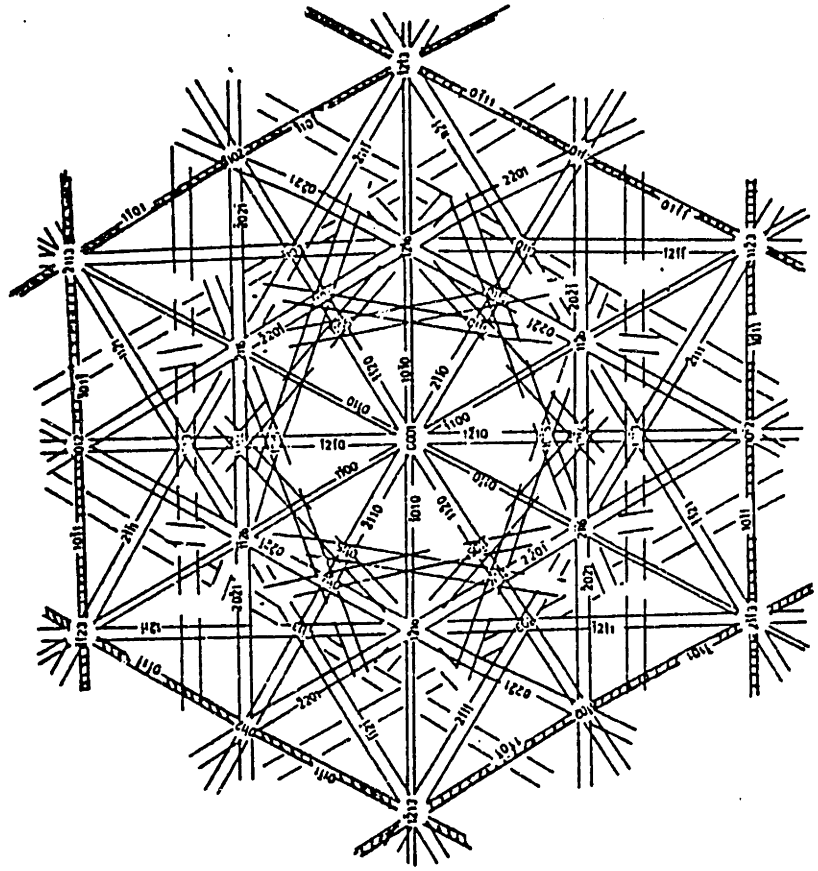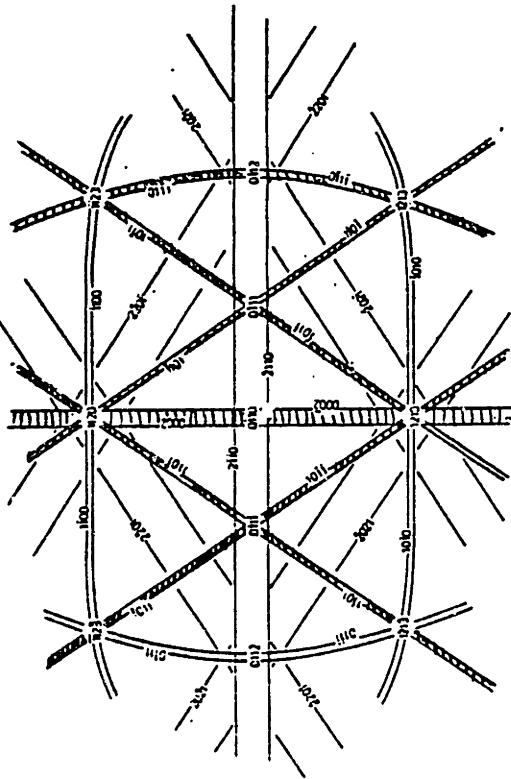
Figure B5 :

KIKUCHI MAP of zircaloy-2
part I
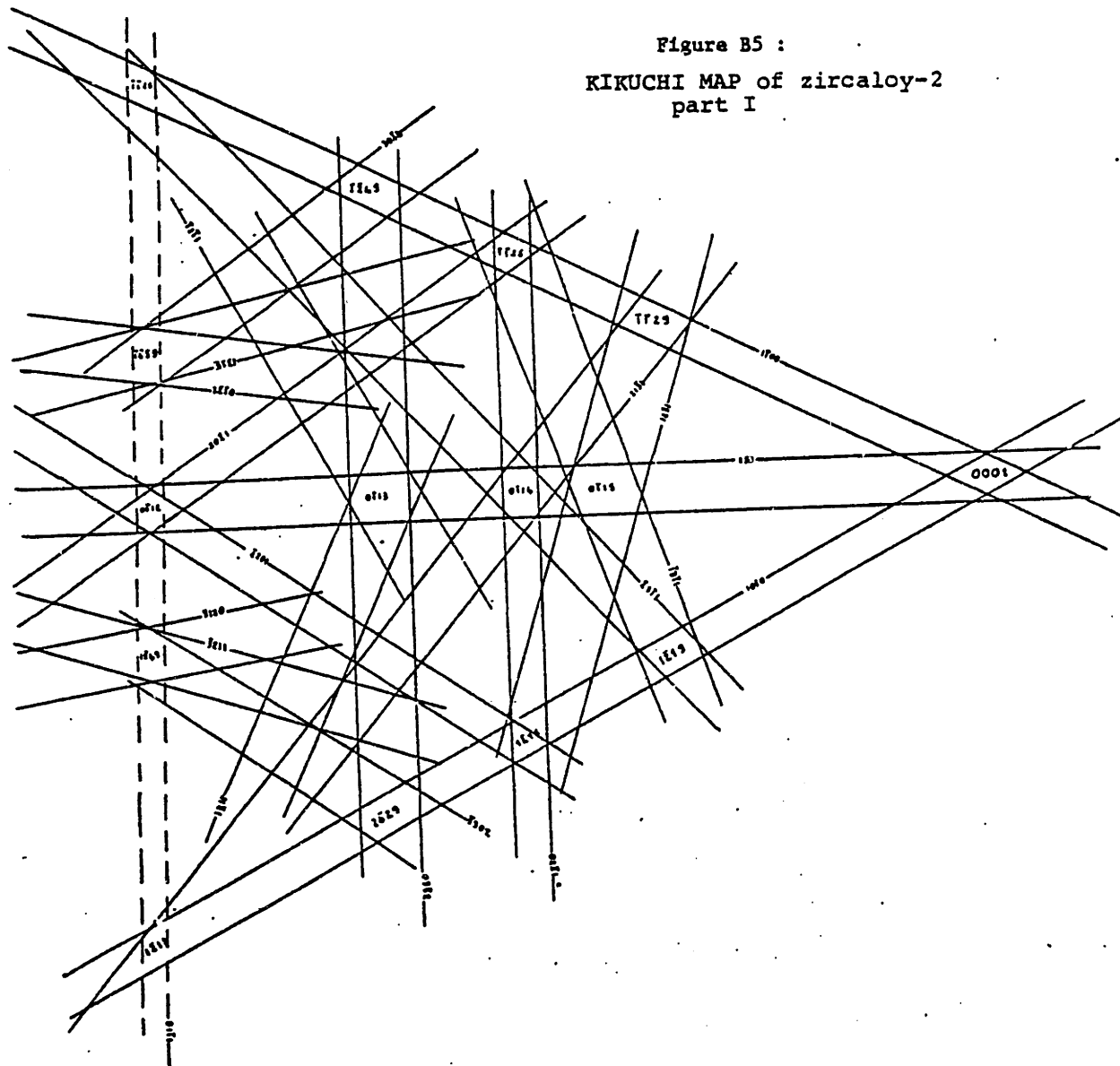
Figure B6 :

KIKUCHI MAP of zircaloy-2
part II
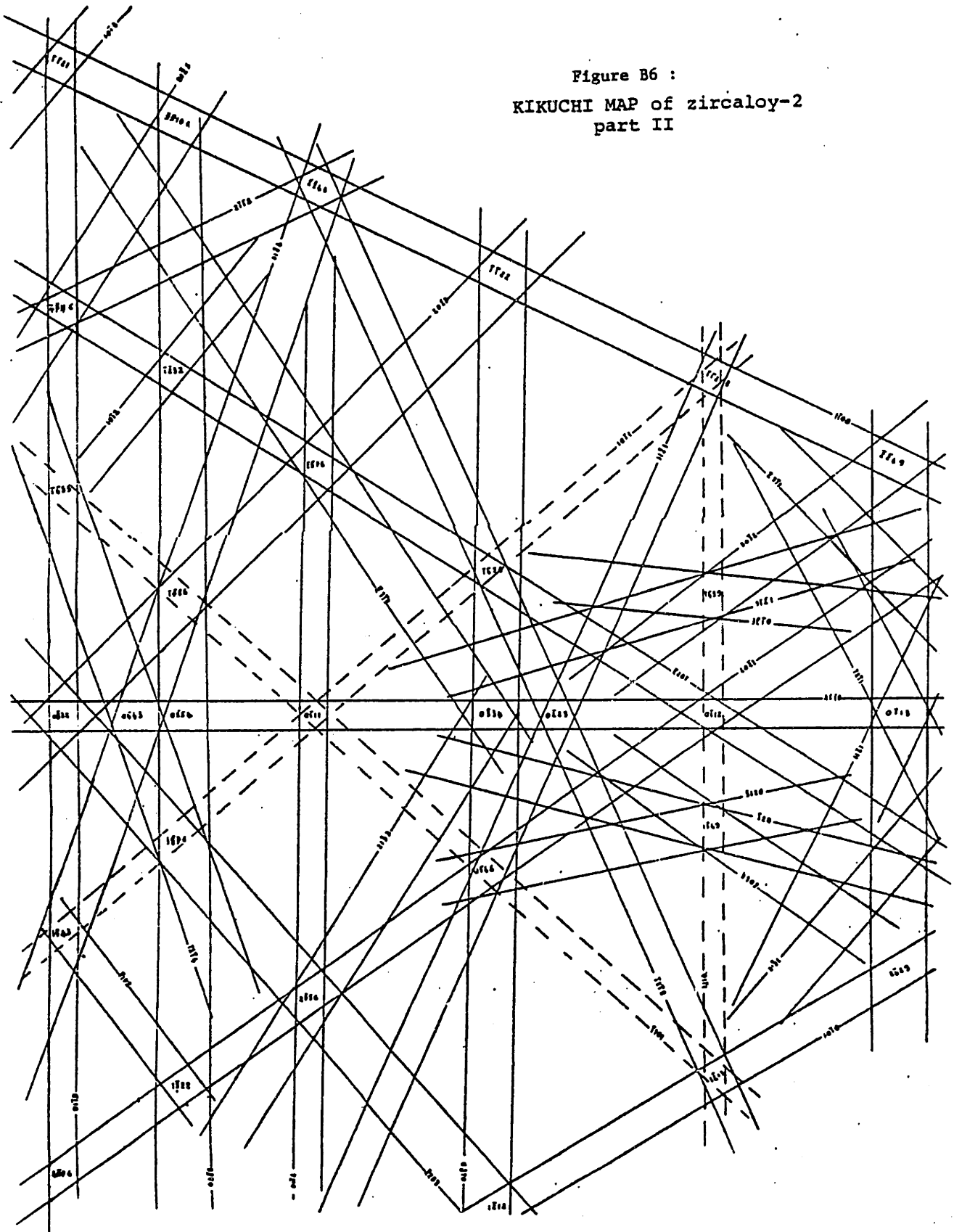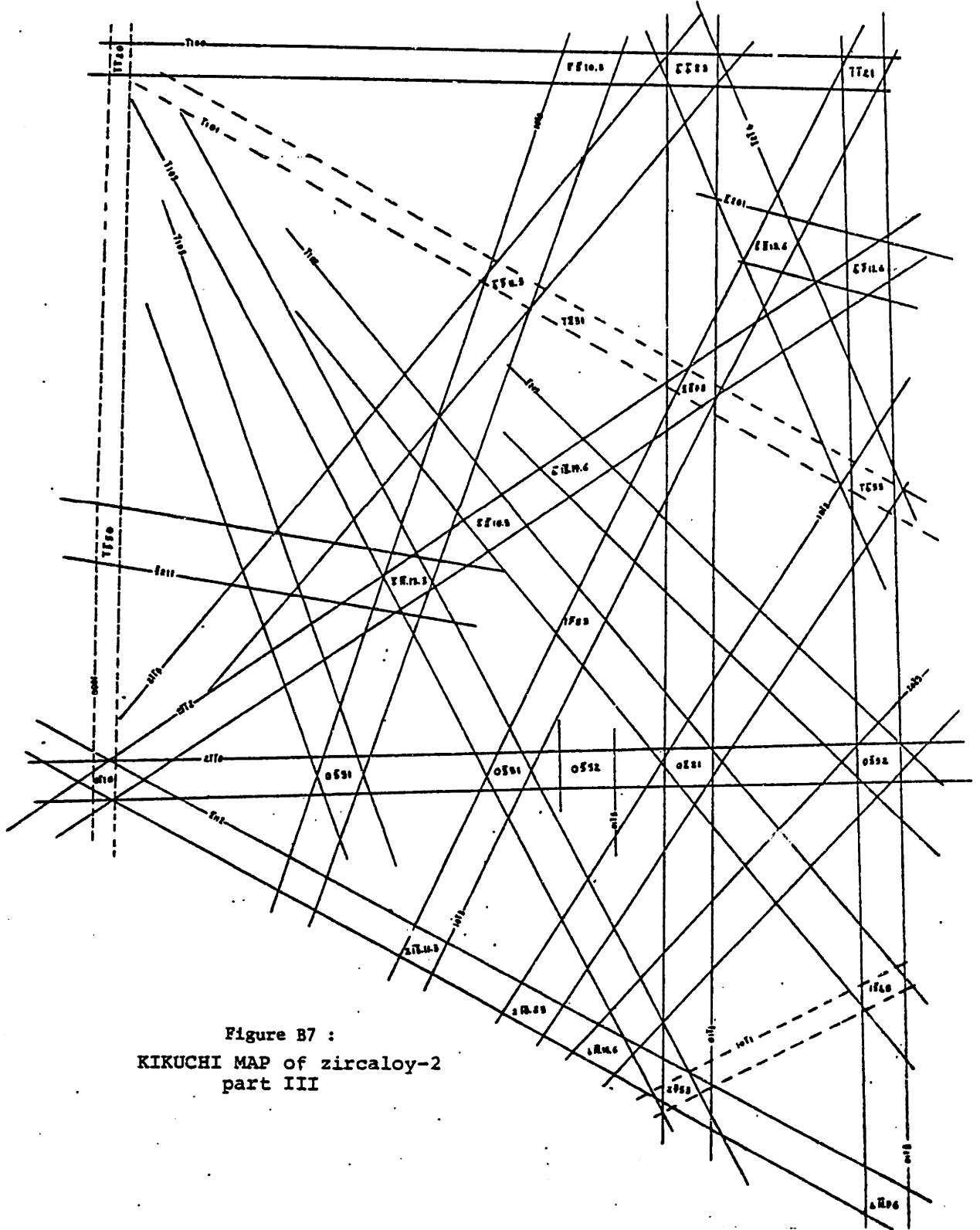
Figure B7 :
KIKUCHI MAP of zircaloy-2
part III

KIKUCHI MAP

for

ZIRCALOY-2

hexagonal structure
c/a=1.593

10°

Figure B8 : Composite Kikuchi map for zircaloy 2. Part I.
(Reduction : 4X)
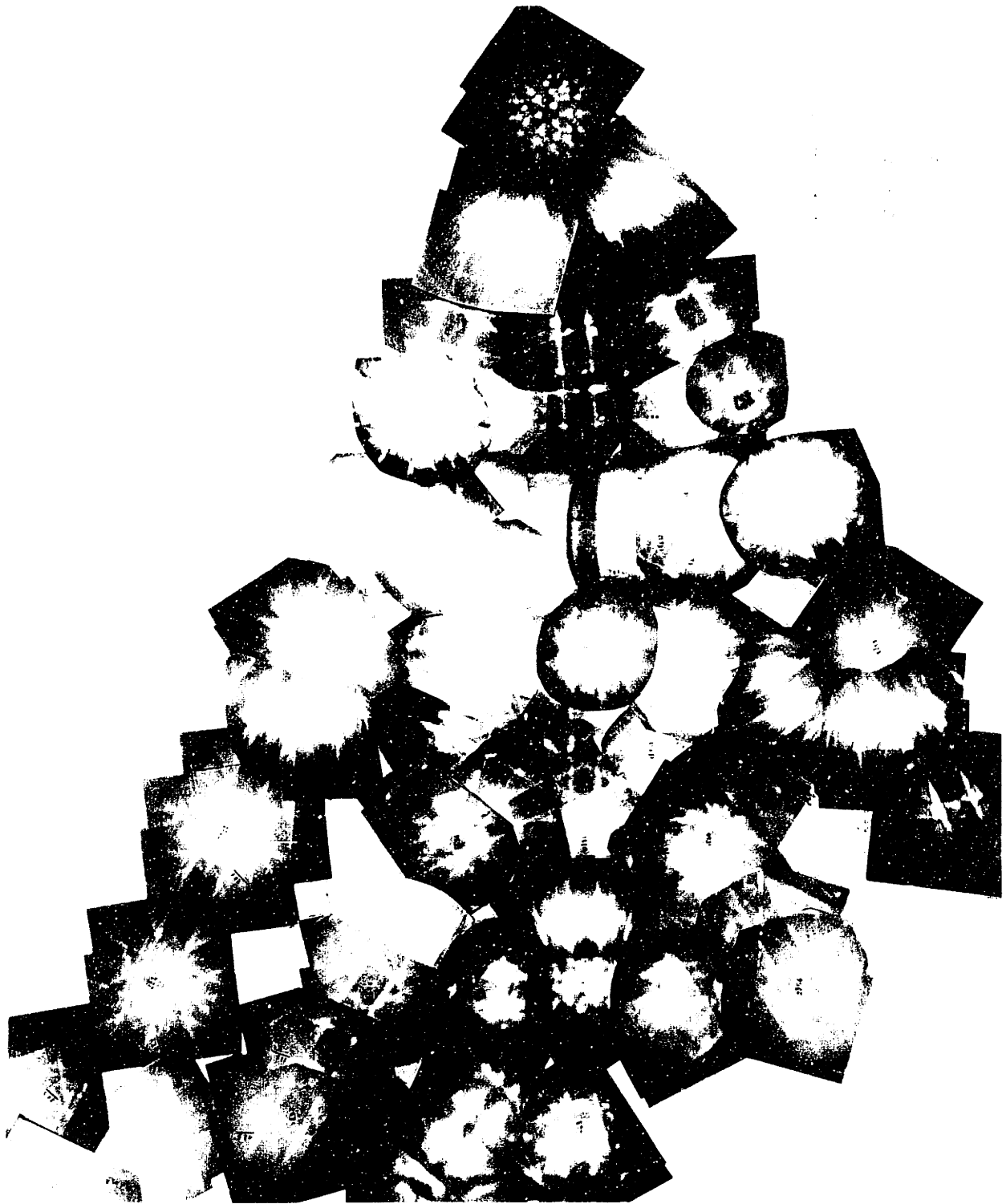
APPENDIX C

STRUCTURE OF ZIRCONIUM COMPOUNDS

The compounds of interest in this work are $ZrCr_2$, Zr_2Ni and Zr_3Si. Tables useful for indexing diffraction patterns and comparisons between interplanar spacings are given in this appendix.

Table C1 – Calculated spacing of the (hkil) plane for hexagonal Zr and $ZrCr_2$.

Table C2 – Twelve of the most densely populated reciprocal lattice plane for $ZrCr_2$ (Similar to Table B for Zr_α).

Table C3 – Calculated interplanar spacing of the (hkl) plane for tetragonal Zr_2Ni.

Table C4 – Calculated interplanar spacing of the (hkl) plane for tetragonal Zr_3Si.

Figure C1 – Some observed electron diffraction patterns corresponding to Zr_3Si.

Table C5 – Calculated interplanar spacing of the (hkl) plane for f.c.c. $ZrCr_2$

Table C1:Calculated$^{\circ}$ interplanar spacing of the (hkil) planes

for hexagonal Zr (c=5.147Å, a=3.232Å)* and

ZrCr$_2$ (c=8.279Å, a=5.079Å)**

$hkil$	Zr_α Å		$ZrCr_2$ Å	
$10\bar{1}0$	2.799	x	4.399	
0002	2.574	x	4.140	x
$10\bar{1}1$	2.459	x	3.884	
$10\bar{1}2$	1.894	x	3.014	
0003			2.760	x
$11\bar{2}0$	1.616	x	2.540	
$10\bar{1}3$	1.463	x	2.338	x
$20\bar{2}0$	1.399	x	2.199	x
$11\bar{2}2$	1.369	x	2.165	x
$20\bar{2}1$	1.350	x	2.126	x
0004	1.287	x	2.070	x
$20\bar{2}2$	1.2295	x	1.942	x
$10\bar{1}4$	1.1691	x	1.873	x
$20\bar{2}3$	1.084	x	1.720	
$21\bar{3}0$	1.058	x	1.662	x
$21\bar{3}1$	1.036	x	1.630	
$11\bar{2}4$	1.007	x	1.604	
$21\bar{3}2$	0.978	x	1.543	x
$10\bar{1}5$	0.966	x	1.550	
$20\bar{2}4$	0.947	x	1.507	x
$30\bar{3}0$	0.933	x	1.466	x
$21\bar{3}3$	0.900	x	1.424	x
$30\bar{3}2$	0.877	x	1.382	x
0006	0.858	x	1.380	
$20\bar{2}5$	0.829	x	1.323	x
$10\bar{1}6$	0.820	x	1.317	
$21\bar{3}4$			1.296	x
$22\bar{4}0$			1.270	x
$11\bar{2}6$			1.212	x

x:observed in X-Ray diffraction *&**
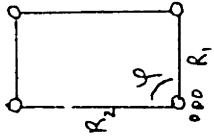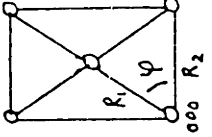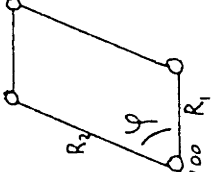
*: ASTM X-Ray card # 5-0665

**: ASTM X-Ray card # 6-0613

$$\circ: \frac{1}{d^2} = \frac{4}{3a^2}\left(h^2+hk+k^2\right) + \frac{1}{c^2}l^2$$

Table C2 : Twelve of the most densely populated reciprocal
lattice planes for $ZrCr_2$.

a=5.079Å   c=8.279Å   c/a= I.630

* ρ (Å²)	36.4	10.68	10.51	9.86	22.34	19.04	14.11	10.67	15.31	11.72	9.20	7.30
$h_2K_2i_2L_2$	$\bar{1}0\,10$	$\bar{1}2\bar{1}1\,•$	$\bar{2}110$	$\bar{2}110$	$10\bar{1}0$	$0\bar{1}\bar{1}1$	$0\bar{1}\bar{1}2$	$0\bar{1}\bar{1}3$	$\bar{1}0\bar{1}1$	$\bar{1}102$	$\bar{1}103$	$\bar{1}321$
d_2 (Å)	4.399	2.428	2.540	2.540	4.399	3.884	3.014	2.338	3.884	3.014	2.338	1.630
$h_1K_1i_1L_1$	$0001\,•$	$10\bar{1}0$	0002	$0\bar{1}\bar{1}1$	$\bar{1}\bar{1}00$	$10\bar{1}0$	$10\bar{1}0$	$10\bar{1}0$	$\bar{1}101$	$10\bar{1}1$	$10\bar{1}1$	$10\bar{1}0$
d_1 (Å)	8.279	4.399	4.140	3.884	4.399	4.399	4.399	4.399	3.884	3.884	3.884	4.399
$\varphi°$	90°	90°	90°	90°	60°	64°	70°	75°	80°	88°	81°	79°
R_2/R_1	1.882	1.812	1.630	1.530	·1.000	1.132	1.459	1.882	1.000	1.285	1.662	2.699
Type	rectangle (R_2, φ, 000, R_1)				cross (R_1, φ, R_2, 000)				parallelogram (R_2, φ, 000, R_1)			
4-indices pole	$\bar{1}2\bar{1}0$	$\bar{1}2\bar{1}6$	$0\bar{1}10$	$0\bar{1}12$	0001	$\bar{1}2\bar{1}3$	$\bar{2}4\bar{2}3$	$\bar{1}2\bar{1}1$	$0\bar{1}11$	$\bar{1}5\bar{4}3$	$\bar{2}7\bar{5}3$	$\bar{1}2\bar{1}9$
3-indices pole	$0\bar{1}0$	$0\bar{1}2$	$\bar{1}20$	$\bar{1}22$	001	$0\bar{1}1$	$0\bar{2}1$	$0\bar{3}1$	$\bar{1}2\bar{1}$	$\bar{1}\bar{3}1$	$\bar{1}\bar{4}\bar{1}$	$0\bar{1}3$

•: occurs by double diffraction

$$*: \rho = \frac{d_1 \cdot d_2}{\sin\varphi}$$

Table C3 : Calculated^O interplanar spacing of the (hkl) planes for tetragonal Zr_2Ni (a=6.499Å c=5.270Å *).

hkl	d_{hkl} Å		hkl	d_{hkl} Å	
1 0 0	6.499		4 1 0	1.576	
0 0 1	5.270		4 0 1	1.553	
1 1 0	4.595		0 2 3	1.545	
1 0 1	4.093		3 3 0	1.532	+
1 1 1	3.464		4 1 1	1.510	+
2 0 0	3.250		1 2 3	1.503	+
2 1 0	2.906		3 2 2	1.488	
2 0 1	2.766		3 3 1	1.471	
0 0 2	2.635	+	4 2 0	1.453	+
2 1 1	2.545	+	2 2 3	1.396	
1 0 2	2.442		4 0 2	1.383	+
2 2 0	2.298	+	0 3 3	1.364	
1 1 2	2.286	+	3 3 2	1.324	+
3 0 0	2.166		0 0 4	1.318	
2 2 1	2.106		1 0 4	1.291	
3 1 0	2.055	+	1 1 4	1.266	
2 0 2	2.047	+	5 2 1	1.176	+
3 0 1	2.004		4 1 3	1.173	+
2 1 2	1.952				
3 1 1	1.915				
3 2 0	1.802				
0 0 3	1.757				
2 2 2	1.732				
3 2 1	1.705				
0 1 3	1.696				
3 0 2	1.673				
1 1 3	1.641				
4 0 0	1.625				
3 1 2	1.621				

+ observed in X-Ray diffraction.*

o : $\dfrac{1}{d^2} = \dfrac{1}{a^2}\left(h^2 + k^2\right) + \dfrac{1}{c^2}\,l^2$

*: A.S.T.M. X.Ray card #I9-857.

$hk\ell$	$d_{hk\ell}$ Å
111	4.163
200	3.605
220	2.549
311	2.174
222	2.081
400	1.803
331	1.654
420	1.612
422	1.472
511 - 333	1.388

$hk\ell$	$d_{hk\ell}$ Å
100	11.01
110	7.785
200	5.505
001	5.450
210	4.924
101	4.884
111	4.465
220	3.893
201	3.873
300	3.670

Table C5 : $ZrCr_2$ Table C4 : Zr_3Si

Calculated° interplanar spacing of the (hkl) planes
for cubic $ZrCr_2$ ($a_o = c_o = 7.21$Å *) and for tetragonal Zr_3Si
($a_o = 11.01$Å $c_o = 5.45$Å (29))

°: $1/d^2 = 1/a^2 (h^2 + K^2) + 1/c^2 L^2$

*: A.S.T.M. X-Ray card # 6-0612.
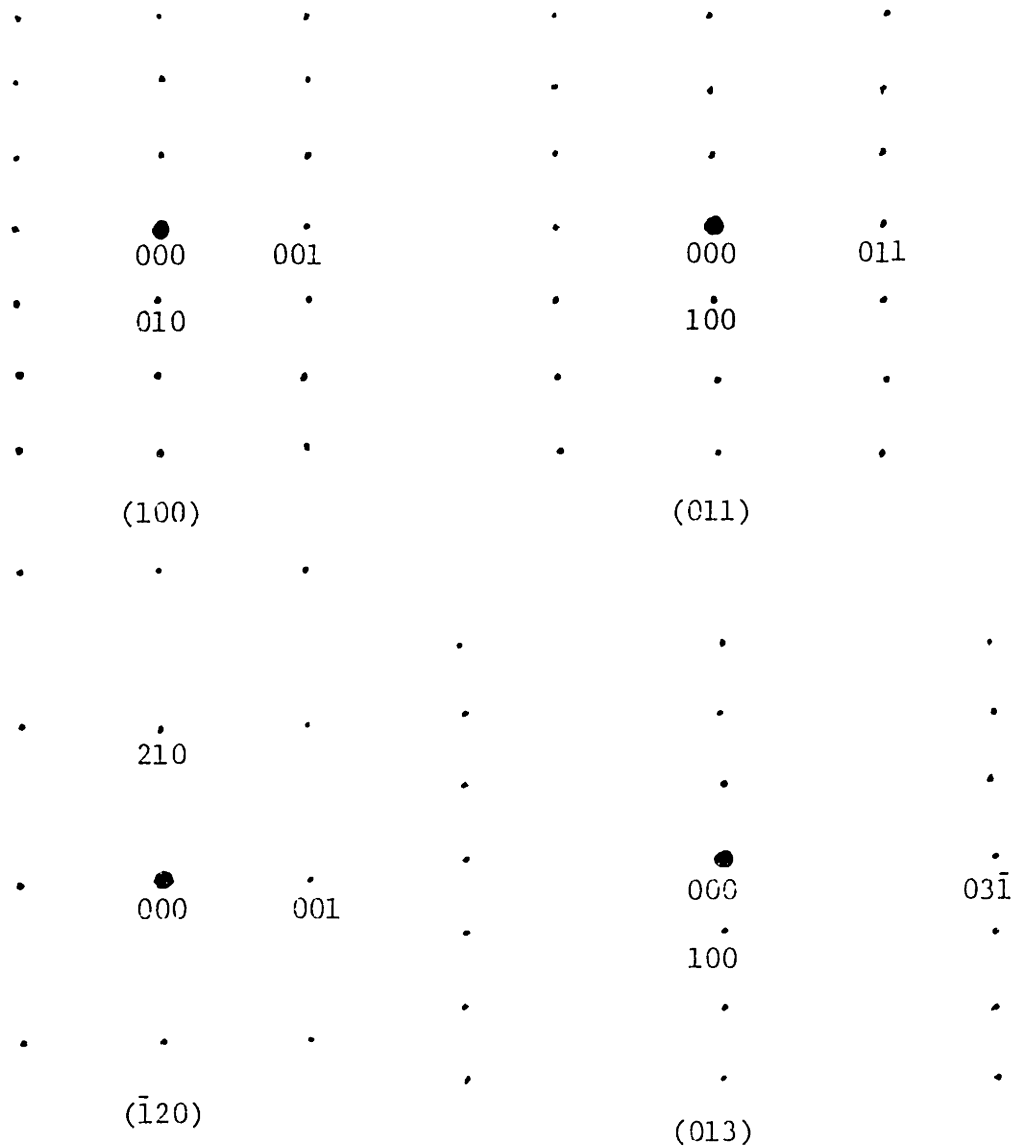
Figure C1 : Some observed electron diffraction patterns
corresponding to tetragonal Zr_3Si.

APPENDIX D

X-RAY DATA OBTAINED IN THE STEM

The computed characteristic indices described in Part III.2c. of this thesis are recorded in the following tables.

The abbreviations used in the "description" column of the tables are:

p: particle

px: particle of type x. x being 1, 2, 3, 4, 5, 6 or 7 as described in Figure 16.

m: matrix

u: inclusion

R: extraction replica

GB: grain boundary

CW: cold worked, stress relieved material.

Each letter of the "spectrum number" corresponds to a different STEM session. For example, B4 is the fourth particle analyzed during the second STEM session.

Table D1 : Computed data for X-Ray analysis.   (I)

spectrum #	time s	BGN crs/sec	Cr	Fe	Ni	Fe/BGN	L/K	Zr	Sn/BGN	description
A1	120	5.23	.2	59	39	6.76	0.77	74	1.83	p 1
A2	120	8.85	2	60	39	3.22	0.90	69	1.29	p 1
A3	60	20.19	53	47	0.3	14.7	1.28	43	1.12	p
A4	60	6.20	54	47	-0.4	11.82	0.85	51	1.12	p 4
A5	80	2.65	55	46	-0.4	5.53	0.45	73	0.98	p
A6	90	2.69	1	56	43	4.29	0.62	83	1.03	p 2
A7	94	6.73	34	99	-33	1.17	1.07	99	1.22	m
A8	120	9.00	40	88	-28	1.23	1.07	99	1.25	m
A9	120	6.10	47	187	-134	1.18	0.97	100	1.14	m
A10	120	5.93	68	49	-17	1.08	0.99	99	1.09	m
A11	80	3.76	53	47	0.3	15.45	0.74	44	1.13	p.
B1	30	8.02	-1	48	52	3.04	0.07	91	1.00	p 7
B2	30	11.9	44	56	0.4	13.04	0.16	62	1.00	p4
B3	30	13.12	1	53	46	7.36	0.14	80	1.03	p7
B4	30	15.60	-1	56	46	5.02	0.13	85	1.11	p7
B5	30	23.64	13	80	7	1.37	0.50	99	1.31	G.B.
B6	30	38.70	0.1	61	38	7.01	0.92	72	1.13	p2
B7	30	34.69	28	89	-17	1.29	1.03	99	1.32	m
B8	30	39.27	36	84	-20	1.27	0.97	99	1.35	m
B9	30	42.77	1	60	40	6.03	0.75	77	1.25	p1
B10	30	45.69	0.4	58	40	7.02	0.72	76	1.33	p1
B11	15	43.20	0.3	59	38	5.39	0.56	84	1.38	p2
B12	15	45.76	48	51	1	7.71	0.87	69	1.38	p7
B13	15	44.47	14	57	30	5.75	0.87	78	1.34	p7
B14	15	43.76	47	52	1	9.08	0.89	64	1.48	p7

Table D1 : cont'd (II)

spectrum #	time s	BGN cts/sec	Cr	Fe	Ni	Fe/BGN	L/K	Zr	Sn/BGN	description
B15	15	37.44	.14	56	30	5.97	0.89	78	1.30	P7
B16	15	40.00	4	58	38	4.78	0.89	83	1.44	P
B17	15	38.50	4	58	38	6.68	0.87	76	1.39	P
B18	15	17.24	2	59	39	8.88	0.80	68	1.21	P3
B19	15	13.20	5	61	34	3.76	0.68	88	1.35	P2
B20	15	22.84	55	45	.2	8.88	1.29	59	1.17	P5
B21	50	7.73	4	59	37	8.85	0.93	71	1.03	P2
B22	20	19.12	48	144	-92	1.25	1.33	99	1.29	m (area)
B23	20	19.93	46	53	0.1	4.62	0.70	83	1.16	P
B24	20	19.30	5	59	36	2.89	0.66	92	1.29	P
B25	20	22.68	3	58	39	5.57	0.68	82	1.22	P (same as B24)
B26	20	23.50	47	53	.0.4	12.08	0.66	59	1.20	P
B27	20	17.70	2	55	43	5.79	0.43	80	1.09	P
B28	20	20.83	1	57	42	9.12	0.43	72	1.25	P (small)
B29	20	33.83	29	58	12	1.39	0.99	98	1.23	m
C1	100	10.44	28	98	-25	1.28	1.00	99	1.00	U
C2	50	7.36	2	56	42	4.02	0.54	86	0.96	P2
C3	50	8.66	2	58	40	6.36	0.77	77	0.96	P
C4	50	7.06	55	44	0.2	11.01	0.55	58	0.91	P5
C5	50	5.45	3	55	42	4.63	0.53	85	0.92	P
C6	50	6.39	3	57	39	5.49	0.60	81	0.96	P (edge)
C7	50	4.28	44	60	-0.3	1.35	0.47	98	1.25	m
C8	50	3.84	7	73	19	1.36	0.20	99	1.11	hole count
C9	50	8.1	53	46	1	10.87	0.51	59	0.87	P2
C10	50	35.54	53	70	-23	1.25	1.13	99	1.40	m

Table D1 : cont'd (III)

spectrum #	time s	BGN cts/sec	Cr	Fe	Ni	Fe/BGN	L/K	Zr	Sn/BGN	description
C11	50	15.07	.69	81	-50	1.17	1.15	99	1.27	m
C12	50	7.23	2	57	41	6.62	0.73	77	0.98	p 2
C13	50	7.96	31	78	-9	1.30	0.91	99	1.26	
C14	50	8.11	1	61	39	8.18	0.92	71	1.00	P 2
C15	50	4.97	57	43	-0.2	10.89	0.52	56	0.96	P 4
C16	50	6.56	55	45	-0.2	13.95	0.74	46	0.93	P
C17	50	4.88	2	58	40	6.22	0.76	78	0.95	P 1
C18	50	9.02	56	44	-0.2	12.60	0.65	51	0.89	P 5
C19	50	8.20	2	57	41	6.23	0.78	78	1.01	P
C20	50	7.78	3	56	41	2.40	0.80	93	1.16	P (etched)
C21	50	6.06	56	43	1	8.88	0.45	63	1.00	P 4.
C22	50	5.48	56	44	-0.3	11.46	0.51	58	0.97	P
C23	50	7.93	1	59	40	6.69	0.83	75	0.97	P l on G.B.
C24	500	8.71	41	82	-22	1.27	0.97	99	1.04	(same as C1)
D1	60	8.43	52	48	1	17.88	0.86	42	1.13	P4
D2	60	7.89	1	60	39	8.93	0.92	69	1.01	P7
D3	60	8.49	52	47	1	17.47	0.79	42	1.08	P7
D4	60	12.78	45	76	-21	1.21	1.11	99	1.26	U
D5	60	13.09	73	56	-29	1.13	1.03	99	1.26	U
D6	60	10.31	2	60	38	4.02	0.84	87	1.41	P 1
D7	60	2.59	55	45	0.1	7.21	0.37	75	1.21	P 5
D8	60	4.95	55	45	-0.2	16.04	0.70	47	1.07	P 5
D9	60	4.33	54	46	-0.4	5.67	0.79	77	1.17	P
D10	60	4.16	53	46	1	6.80	0.80	73	1.13	P
D11	60	5.81	52	48	0.3	17.38	0.78	43	1.11	P 7

Table D1 : cont'd ($\underline{IV}$)

spectrum #	time s	BGN cts/sec	Cr	Fe	Ni	Fe/BGN	L/K	Zr	Sn/BGN	description
D12	60	5.45	·3	58	39	9.94	0.87	69	1.07	P7
D13	60	4.07	52	47	1	18.19	0.65	46	1.07	P7
D14	60	4.70	1	58	40	7.65	0.82	76	1.06	P1 on G.B.
D15	60	14.24	75	40	-16	1.05	1.83	100	1.46	m
E1	60	3.61	55	45	1	10.73	0.83	60	1.01	P7
E2	60	2.70	2	57	41	6.13	0.64	81	0.85	P7
E3	60	4.46	35	70	-5	1.10	1.06	100	1.37	m
F1	60	6.71	55	45	0.2	24.12	2.00	20	0.91	R
F2	60	7.48	54	46	1	24.08	1.89	20	1.03	R
F3	30	13.22	56	43	0.2	21.37	1.82	21	0.90	R
F4	20	23.98	56	44	0.4	23.03	1.76	20	1.05	R
F5	20	8.63	54	45	0.2	20.60	1.97	21	0.95	R
F6	20	8.03	55	44	1	25.12	1.71	21	1.11	R
F7	20	11.50	54	45	1	25.65	1.86	20	0.97	R
F8	20	9.23	54	45	0.4	26.56	1.88	20	1.12	R
F9	20	10.90	55	44	1	23.90	1.87	21	1.01	R
F10	20	4.40	56	44	0.2	21.15	1.82	20	0.90	R
F11	20	4.03	54	45	0.5	26.75	1.87	20	0.99	R
F12	20	7.43	55	44	0.2	25.83	1.87	20	1.02	R
G1	50	31.80	53	47	-0.4	23.83	1.16	25	1.15	P6
G2	50	2.56	2	56	42	13.04	1.83	54	1.00	P3
G3	50	4.12	55	45	-0.1	24.10	1.86	22	0.91	P
G4	50	0.68	57	42	1	30.68	1.90	23	0.87	P5
G5	50	5.02	2	59	39	12.13	1.43	57	1.25	P7
G6	50	5.75	54	46	0.3	13.21	1.71	45	1.21	P7

Table D1 : cont'd($\underline{Y}$)

spectrum #	time s	EGN	Cr	Fe	Ni	Fe/BGN	L/K	Zr	Sn/BGN	description
G7	50	174	.57	44	-0.2	25.06	1.63	23	0.75	p7
G8	50	4.46	55	44	0.4	27.36	1.63	23	1.02	p7
G9	50	4.42	2	59	38	10.57	1.30	59	1.05	p7
G10	50	3.41	56	44	0.3	24.98	1.69	23	1.00	p7
G11	50	5.97	2	58	39	12.21	1.55	57	0.98	p2
G12	50	4.46	2	58	40	12.82	1.91	53	1.05	p
G13	50	4.46	2	58	40	11.54	1.48	56	1.07	p7
G14	50	3.06	54	45	0.2	25.97	1.48	24	1.25	p7
G15	20	8.83	56	44	-0.1	9.63	1.41	56	1.33	p7
G16	20	3.28	57	44	-0.1	23.18	1.69	24	0.95	p7
G17	20	3.45	54	46	-0.2	20.87	1.78	29	0.89	p
G18	20	6.15	54	46	-0.3	11.01	1.40	51	1.53	p7
G19	20	6.50	56	44	-0.2	10.84	1.38	51	1.51	p
G20	50	3.55	3	52	46	11.06	1.80	53	0.94	CW p3
G21	25	7.59	2	53	45	11.53	1.35	55	1.10	CW p3
G22	50	4.14	57	43	0.2	22.90	1.77	25	1.12	CW P
G23	25	5.66	61	39	0.2	19.46	1.79	27	1.25	CW P
G24	25	8.10	55	44	1	20.13	1.71	27	1.09	CW P
G25	25	6.78	52	46	2	22.54	1.75	27	1.03	CW P
G26	25	3.46	60	40	-0.2	8.00	1.77	56	1.06	CW P
G27	25	3.26	58	42	-0.2	6.99	1.54	63	1.19	CW P
G28	50	4.01	45	36	19	1.12	1.26	99	1.38	CW m
G29	25	42.18	47	47	6	1.27	1.03	98	1.51	CW m (thicker)
G30	25	25.56	31	50	19	1.33	1.09	98	1.20	CW U
G31	25	16.18	53	48	-1	1.22	1.71	98	1.07	CW U

Table D1 : cont'd (VI)

spectrum #	time s	BGN	Cr	Fe	Ni	Fe/BGN	L/K	Zr	Sn/BGN	description
G32	25	5.14	.2	49	50	9.53	0.87	63	1.46	CW P3
G33	25	15.02	73	83	-55	1.16	1.61	99	1.05	U
G34	25	20.43	2	60	38	7.18	1.49	68	117	P1
G35										P
G36	55	11.10	1	62	37	4.58	1.59	81	1.15	P2

APPENDIX E

CHARACTERISTICS OF THE TEM PHILIPS EM300

The camera constant was determined with a gold sputtered film and with MoO_3 single crystals. The rotation between image and electron diffraction pattern was measured using the edge of MoO_3 single crystals. Pictures of the same area of a specimen at different knob settings were used to measure the magnification. The determination of the magnification by A. Garratt-Reed was supposed correct at the 15 Mag. knobs setting. These characeristics of the microscope are given Figure E1.

Figure E1 : Characteristic parameters of the TEM Philips EM300
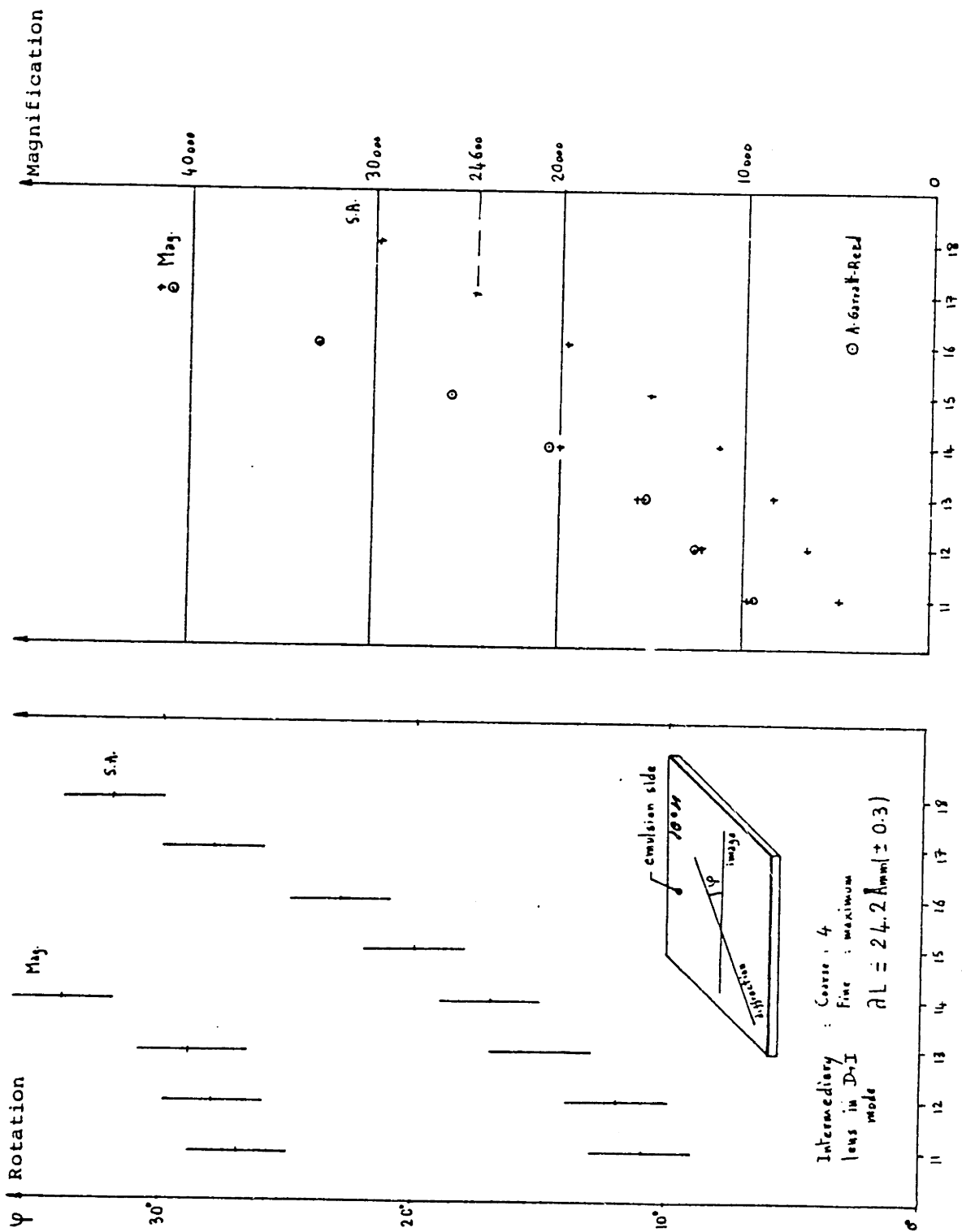
Magnification knob setting (intermediary lens in Mag. & S.A. mode)

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