CHAPTER - III

RESULTS

3.1 INTRODUCTION :

Porous Al_2O_3 films are potential candidates as moisture sensors in optical coating assembly and in microelectronic circuits. The study of refractive index, adhesion, D.C. resistance, IR, XRD measurements for various thickness range of porous Al_2O_3 films and investigations regarding the effect of moisture and heat on these films would help in fabrication of a better sensing device.

In this work thickness was measured by Tolansky technique, Abele's method for refractive index measurement, Direct pull off technique for adhesion and two probe method for D.C.resistance.

3.2 GENERAL PLAN IN THE PRESENT WORK :

The present work deals with refractive index, adhesion, D.C.resistance,IR spectra of the porous Al_2O_3 films obtained by two different methods as already explained in chapter II. The films were studied over the thickness range 400-1500 A°. For all the films the initial readings i.e. fresh films were taken in air immediately after formation of films, expect for adhesion measurements which needs a curing time of araldite of 24 hours.

The parameters measured were

1] Refractive index - The spectrometer angle at which film-glass demarcation disappears.

2] Adhesion - The spring balance reading at film substrate interface breaking.

3] IR spectra - Changes in intensity of absorption band.

4] D.C. resistance - Change in the current reading using picoammeter.

3.3 DATA OF REFRACTIVE INDEX :

3.3.1 FRESH FILMS :

Fig.3.3.1(a) gives the scatter diagram of refractive index as a function of thickness for hot water oxidised and steam oxidised Al_2O_3 films. All the experimental data are plotted in this graph. From the fig. it is seen that sample to sample scatter is very much less in steam oxidised films as compared to hot water oxidised films. A general thickness independent refractive index trend is shown for both the types of Al_2O_3 films.

The average values of refractive index of fresh films are plotted in Fig.3.3.1(b). From the figure it is seen that Al_2O_3 films obtained by oxidation of aluminium in presence of steam is higher than that of films obtained by oxidation in hot water. The refractive index does not

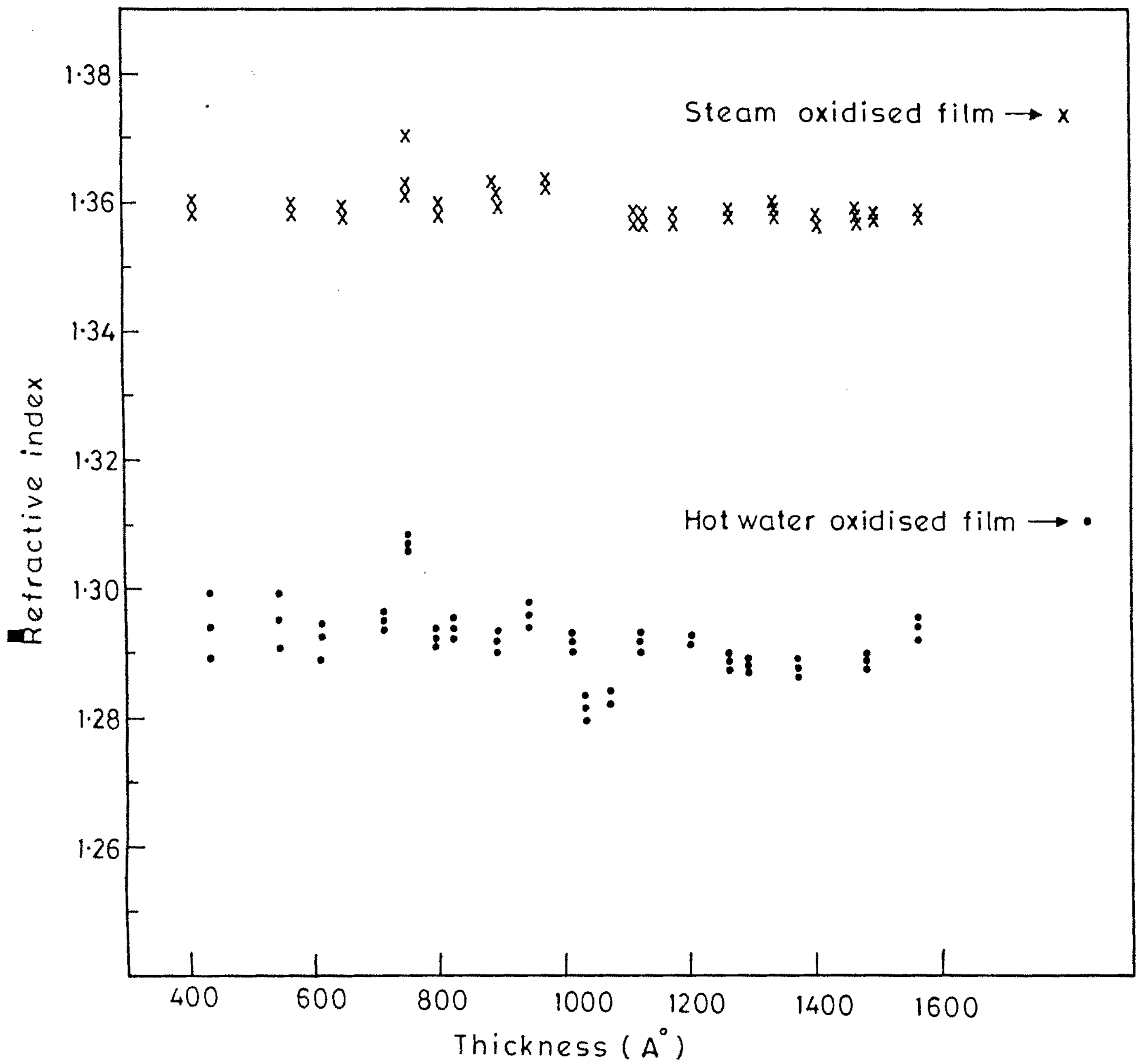

Fig.3·3·1 (a) – SCATTERED DIAGRAM OF REFRACTIVE INDEX VERSUS THICKNESS (FRESH FILM).

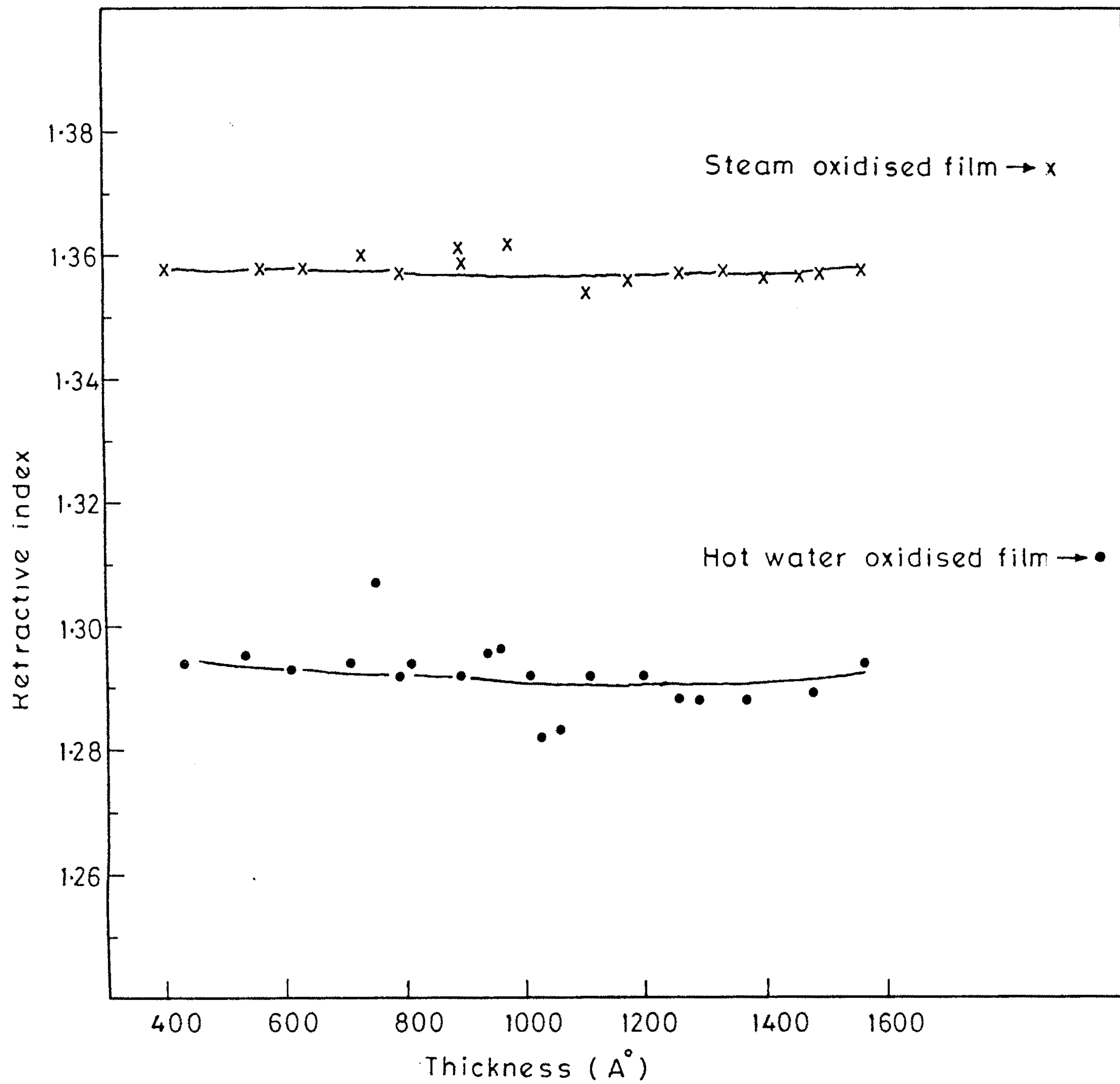

Fig. 3·3·1 (b) - REFRACTIVE INDEX OF FRESH Al_2O_3 FILMS FORMED BY STEAM OXIDATION AND HOT WATER OXIDATION.

show any specific dependence on thickness. Similar trends also observed in Fig.3.3.1(a).

3.3.2 POROSITY DATA :

The porosity of Al_2O_3 films were obtained from using the packing density formula given in equation 1.2.4. Fig.3.3.2(a) and fig.3.3.2(b) gives the packing density and porosity plots respectively for both types of Al_2O_3 films. It is seen from figures that both porosity and packing density does not depend on thickness. It is also seen that Al_2O_3 films obtained by steam oxidation have higher packing density and lower porosity than those obtained by hot water oxidation.

3.3.3 STUDY OF AMBIENT EFFECTS ON POROUS Al_2O_3 FILMS :

As indicated in Chapter II the films were exposed to moisture, sequential effect (fresh film-heat 40°C - 65% moisture - 98% moisture - room temperature), and heat 120°C. All the refractive index measurements were taken in air.

3.3.3.1 EFFECT OF SATURATED MOISTURE :

Fig.3.3.3.1 gives the changes in refractive index as a function of thickness for both steam oxidised and hot water oxidised films, after exposure to saturated moisture (98%) for 3 hours. From the fig. it is seen that the refractive index decrease for both type of films, but

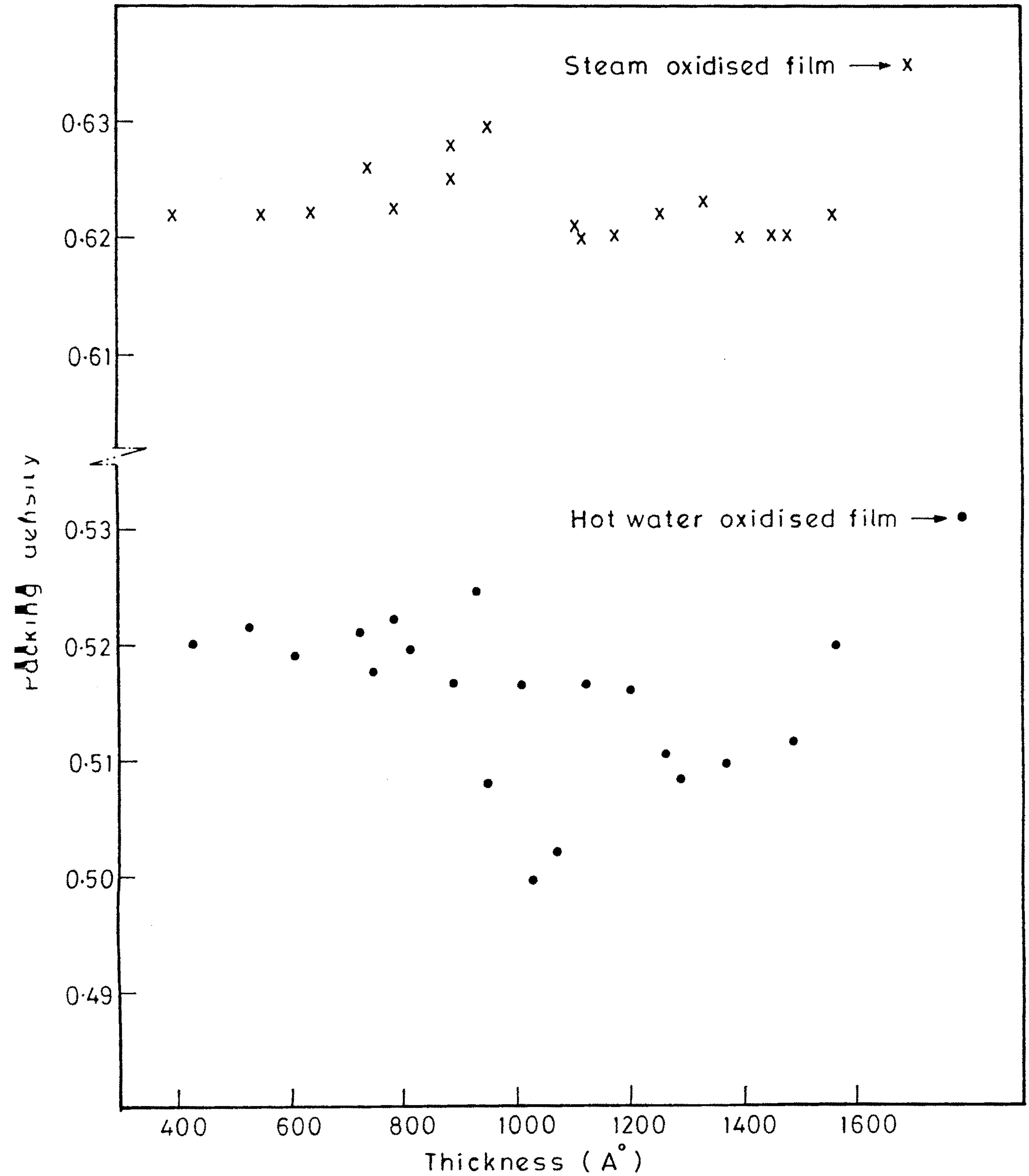

Fig. 3·3·2 (a) – PACKING DENSITY OF FRESHLY PREPARED Al_2O_3 FILMS BY STEAM OXIDATION AND HOT WATER OXIDATION.

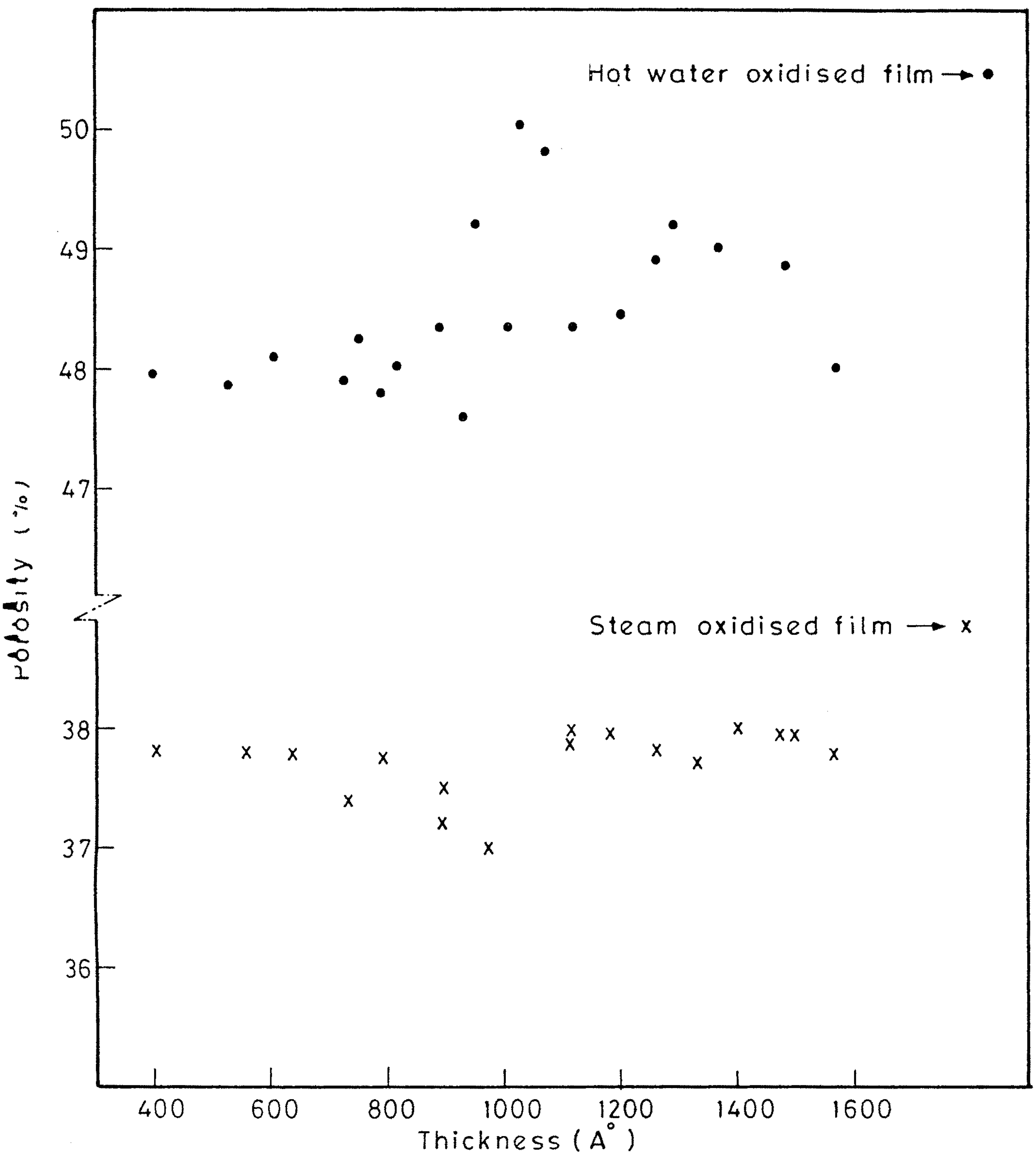

Fig. 3·3·2 (b) – POROSITY OF FRESHLY PREPARED Al_2O_3 FILMS BY STEAM OXIDATION AND HOT WATER OXIDATION.

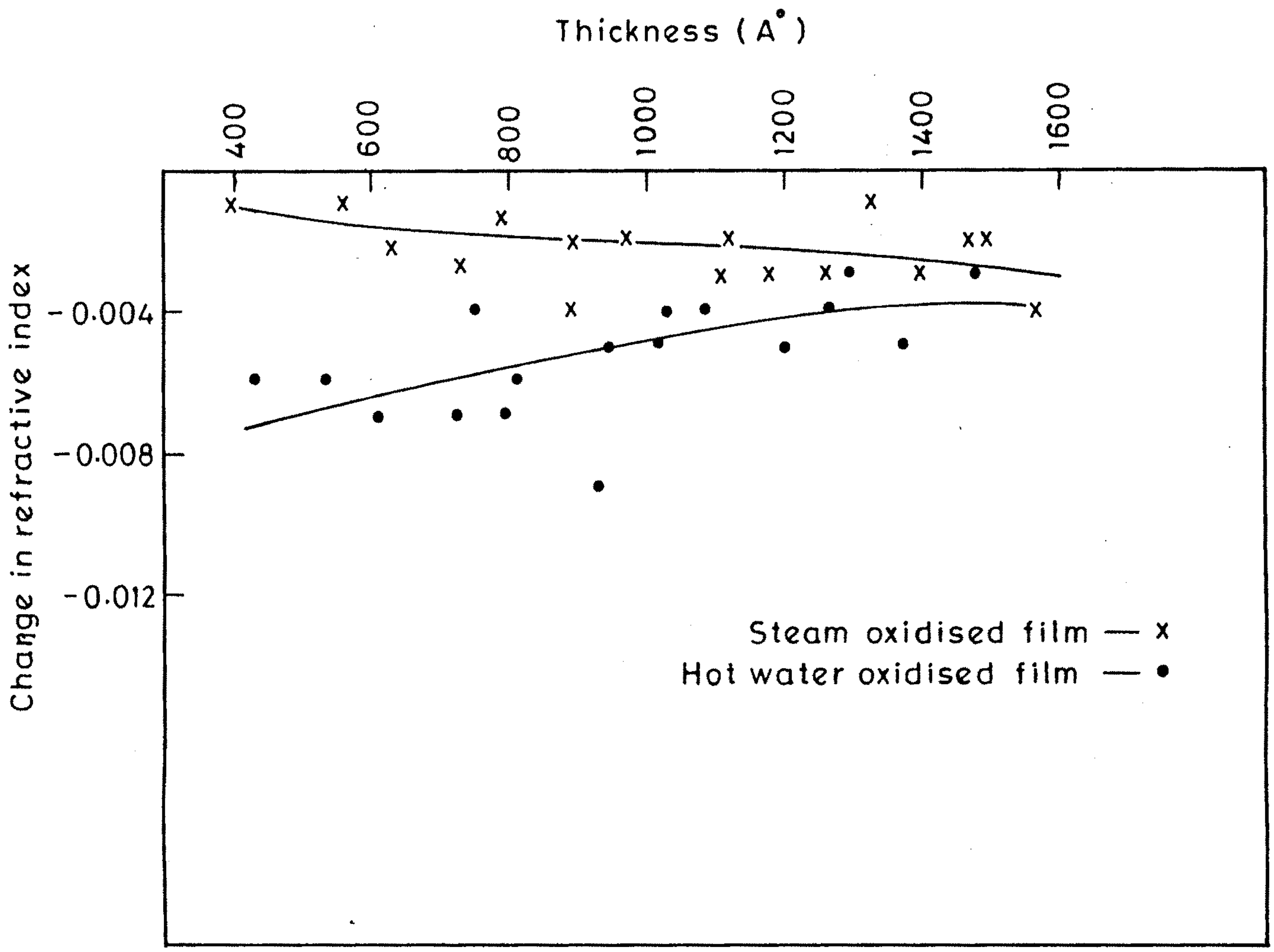

Fig. 3·3·3·1 CHANGE IN REFRACTIVE INDEX ON EXPOSURE TO SATURATED MOISTURE OF Al_2O_3 FILMS FORMED BY STEAM OXIDATION AND HOT WATER OXIDATION.

the steam oxidised films show less decrease than hot water oxidised films.

The change in packing density after moisture exposure is represented in Fig.3.3.3.1(a). From the fig. it is seen that the changes of packing density of steam oxidised films are lesser than those of hot water oxidised films. Also the changes are more for hot water oxidised films of lower thickness whereas in steam oxidised films such type of effect is not observed.

3.3.3.2 EFFECT OF REPEATED SEQUENTIAL EXPOSURES :

To understand the moisture sensing property of the films, the films were exposed to the following sequence (fresh film - heat 40°C - 65% moisture - 98% moisture - room temperature).

After the fresh film measurement were taken, the films were heated to 40°C to ensure that the moisture adsorbed during film formation is removed. The temperature of 40°C was chosen as it is not away from room temperature and not very much high for permanent change to occur but sufficient enough for moisture removal.

The data of refractive index change due to above sequence is given in fig.3.3.3.2. From the figure it is seen that the effect of 40°C heat is to decrease the refractive index in both the types of films. The decrease being more

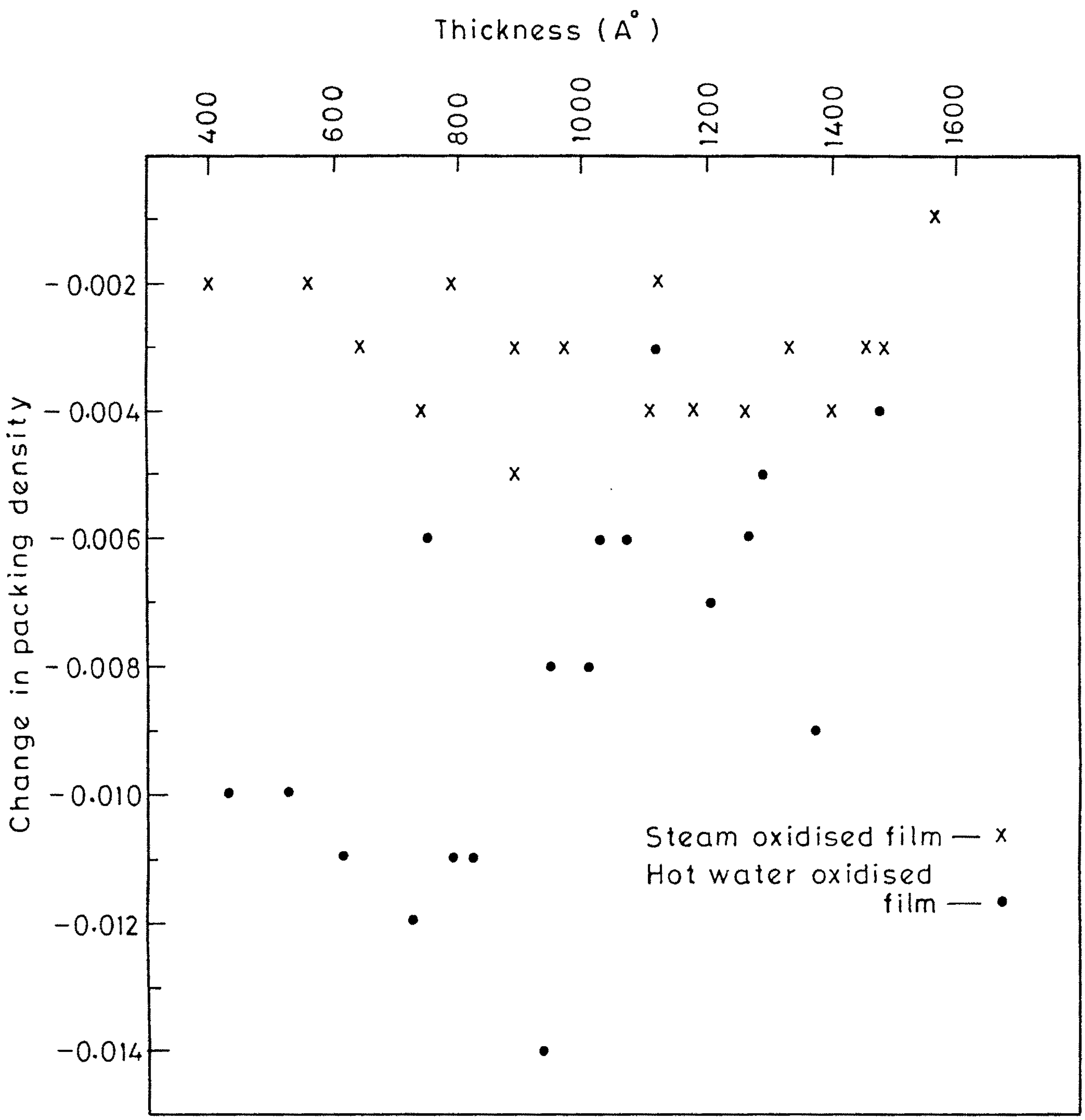

Fig. 3·3·3·1 (a)– CHANGE IN PACKING DENSITY ON EXPOSURE TO SATURATED MOISTURE VERSUS THICKNESS OF Al_2O_3 FILM FORMED BY STEAM OXIDATION AND HOT WATER OXIDATION.

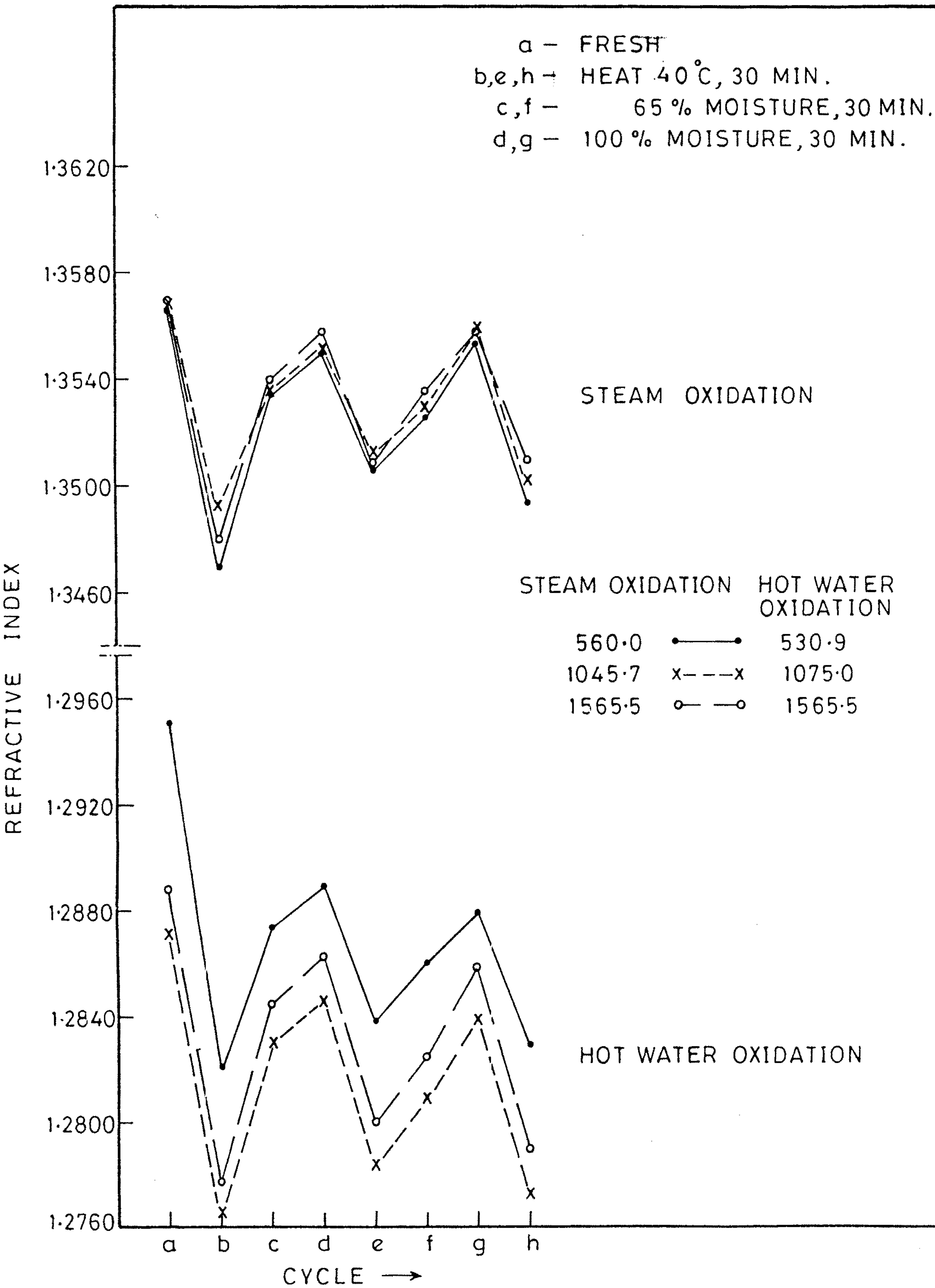

Fig. 3·3·3·2-REFRACTIVE INDEX OF THIN Al_2O_3 FILMS ON EXPOSURE TO HEAT - MOISTURE CYCLE FORMED BY STEAM OXIDATION AND HOT WATER OXIDATION OF ALUMINIUM.

for hot water oxidised films. On exposure to 65% moisture, the refractive index again increases and further exposure to 98% moisture has the effect of increasing refractive index. But in both the cases the refractive index is lesser than the fresh film values. These type of changes is repeated on repeating the sequence. The sequence is repeated 3 times.

3.3.3.3 EFFECT OF HEAT (120°C) :

Fig.3.3.3-3shows the change of refractive index versus thickness after heating the film at 120°C for 3 hours. From the graph it is seen that there is decrease in refractive index for both the steam oxidised and hot water oxidised films, the decrease being more for steam oxidised films. The hot water oxidised films showing more thickness dependent randomness than steam oxidised films. As compared to fig.3.3.3.2 for heating to 40°C the changes obtained after heating to 120°C are considerably higher indicating some different phenomenon occuring during heating.

The consolidated refractive index and packing density data of all the ambient effects is given in tables 3.3(a), 3.3(b), and 3.3.(c)

3.4 ADHESION :

3.4.1 FRESH FILMS :

All the adhesion data of fresh films both steam oxidised and hot water oxidised are given in Fig.3.4.1.

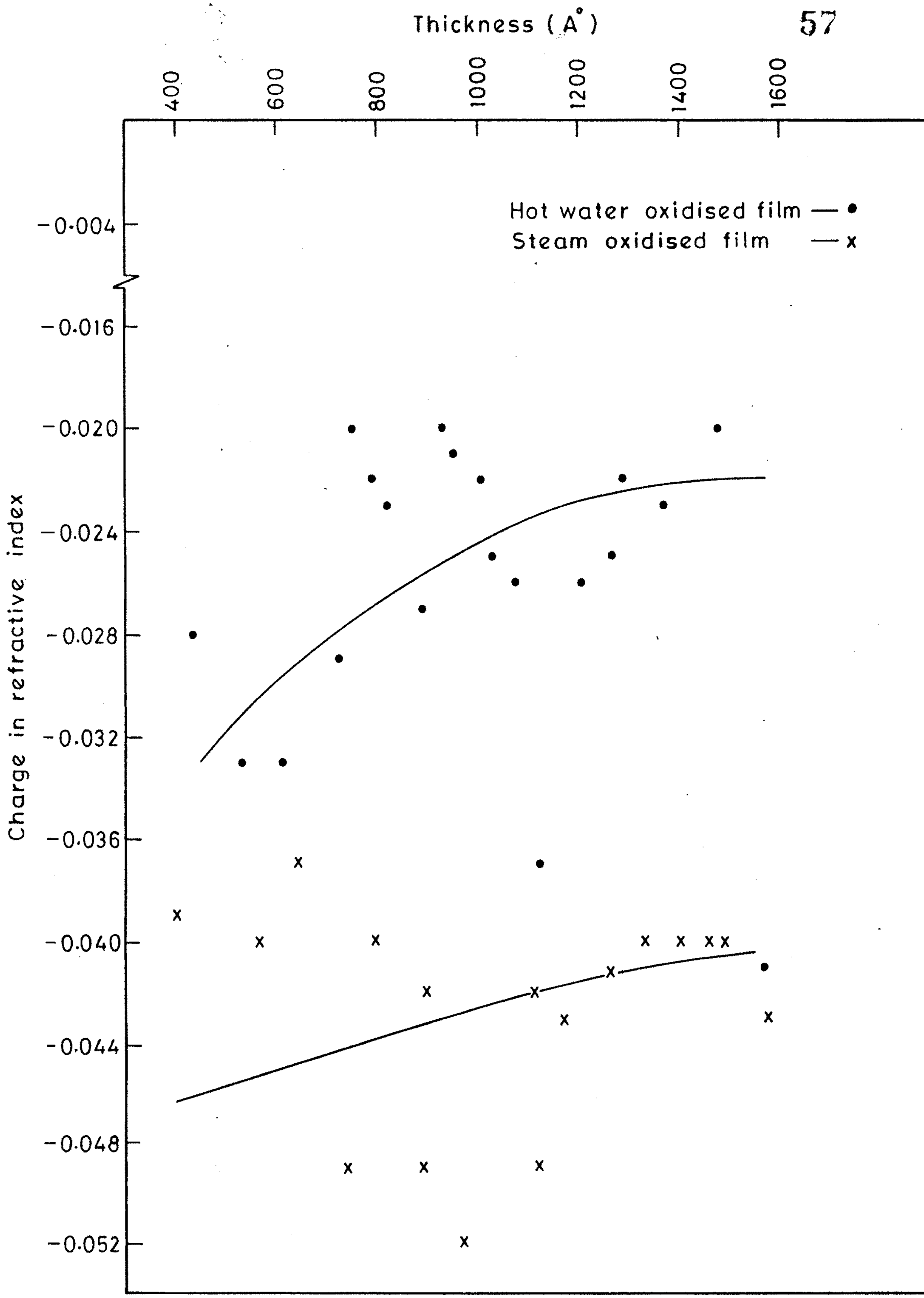

Fig. 3·3·3·3 – CHANGE IN REFRACTIVE INDEX ON EXPOSURE TO HEAT (120°C) OF Al_2O_3 FILM FORMED BY STEAM OXIDATION AND HOT WATER OXIDATION.

Table 3.3 (a)

Refractive index (μ) and packing density (P.D.) data of Steam oxidised Al_2O_3 thin films.

Thickness	Steam Oxidised Films					
A°	Fresh film		Saturated moisture film		Heated film 120°C	
	μ	P.D'	μ	P.D.	μ	P.D.
400.0	1.358	0.622	1.356	0.620	1.319	0.560
560.0	1.358	0.622	1.356	0.620	1.318	0.558
636.6	1.358	0.622	1.355	0.619	1.321	0.563
736.8	1.361	0.626	1.358	0.622	1.311	0.548
790.5	1.358	0.623	1.357	0.620	1.318	0.558
890.9	1.362	0.628	1.360	0.625	1.320	0.562
892.2	1.360	0.625	1.356	0.620	1.310	0.547
971.4	1.363	0.630	1.361	0.626	1.310	0.546
1110.1	1.357	0.621	1.355	0.617	1.316	0.555
1120.0	1.357	0.620	1.355	0.617	1.307	0.542
1182.2	1.357	0.620	1.354	0.616	1.313	0.552
1260.0	1.358	0.622	1.355	0.617	1.316	0.556
1333.3	1.358	0.622	1.357	0.620	1.318	0.559
1400.0	1.357	0.620	1.354	0.616	1.316	0.557
1466.0	1.357	0.621	1.355	0.617	1.317	0.557
1487.0	1.357	0.620	1.355	0.617	1.317	0.557
1565.5	1.358	0.622	1.357	0.620	1.315	0.555

Table 3.3(b)

Refractive index (μ) and packing density (P.D.) data of hot water oxidised Al_2O_3 thin films.

Thickness	Hot Water Oxidised Films					
A°	Fresh film		Saturated moisture film		Heated film 120°C	
	μ	P.D.	μ	P.D.	μ	P.D.
433.4	1.294	0.520	1.288	0.510	1.266	0.474
530.9	1.295	0.522	1.289	0.512	1.262	0.467
610.6	1.293	0.519	1.287	0.508	1.260	0.464
725.9	1.295	0.521	1.288	0.509	1.266	0.474
750.1	1.293	0.519	1.289	0.512	1.273	0.485
789.6	1.295	0.521	1.289	0.512	1.273	0.485
816.0	1.293	0.519	1.288	0.509	1.270	0.482
890.9	1.292	0.516	1.290	0.513	1.265	0.472
933.3	1.297	0.524	1.288	0.509	1.277	0.492
950.8	1.287	0.508	1.282	0.500	1.266	0.474
1008.0	1.292	0.516	1.287	0.508	1.269	0.480
1030.0	1.282	0.500	1.278	0.493	1.256	0.458
1070.0	1.283	0.502	1.279	0.496	1.257	0.459
1120.0	1.292	0.516	1.289	0.511	1.255	0.455
1200.0	1.292	0.516	1.287	0.508	1.265	0.473
1265.0	1.288	0.509	1.285	0.504	1.264	0.470
1290.0	1.287	0.508	1.283	0.503	1.264	0.470
1370.0	1.288	0.509	1.283	0.503	1.265	0.472
1480.0	1.289	0.512	1.286	0.507	1.269	0.480
1565.5	1.294	0.520	1.289	0.511	1.253	0.452

Table 3.3.(c)

Refractive Index (μ) and Packing Density (P.D.) data for sequencial exposure of Steam oxidiesd and Hot water oxidised Al_2O_3 thin films.

Steam Oxidation

Thickness	560.0 A°		1045.7 A°		1565.5 A°	
Sequence	μ	P.D.	μ	P.D.	μ	P.D.
a) Fresh film	1.357	0.620	1.357	0.620	1.357	0.620
b) Heat 40°C, 30 min.	1.347	0.605	1.349	0.608	1.348	0.606
c) Moisture 65%, 30 min.	1.353	0.615	1.354	0.616	1.354	0.616
d) Moisture 100%, 30 min.	1.355	0.618	1.355	0.618	1.356	0.619
e) Heat 40°C, 30 min.	1.351	0.610	1.351	0.610	1.351	0.610
f) Moisture 65%, 30 min.	1.353	0.615	1.353	0.615	1.354	0.616
g) Moisture 100%, 30 min.	1.355	0.618	1.356	0.619	1.357	0.620
h) Heat 40°C, 30 min.	1.349	0.608	1.350	0.610	1.351	0.610

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Hot Water Oxidation

Thickness	530.9 A°		1075.0 A°		1565.5 A°	
Sequence	μ	P.D.	μ	P.D.	μ	P.D.
a) Fresh film	1.295	0.522	1.287	0.509	1.289	0.512
b) Heat 40°C, 30 min.	1.282	0.501	1.277	0.491	1.278	0.493
c) Moisture 65%, 30 min.	1.288	0.509	1.283	0.502	1.285	0.504
d) Moisture 100%, 30 min.	1.289	0.512	1.284	0.505	1.286	0.507
e) Heat 40°C, 30 min.	1.284	0.503	1.278	0.494	1.280	0.497
f) Moisture 65%, 30 min.	1.286	0.507	1.281	0.499	1.283	0.501
g) Moisture 100%, 30 min.	1.288	0.510	1.284	0.504	1.286	0.506
h) Heat 40°C, 30 min.	1.283	0.502	1.277	0.493	1.270	0.495

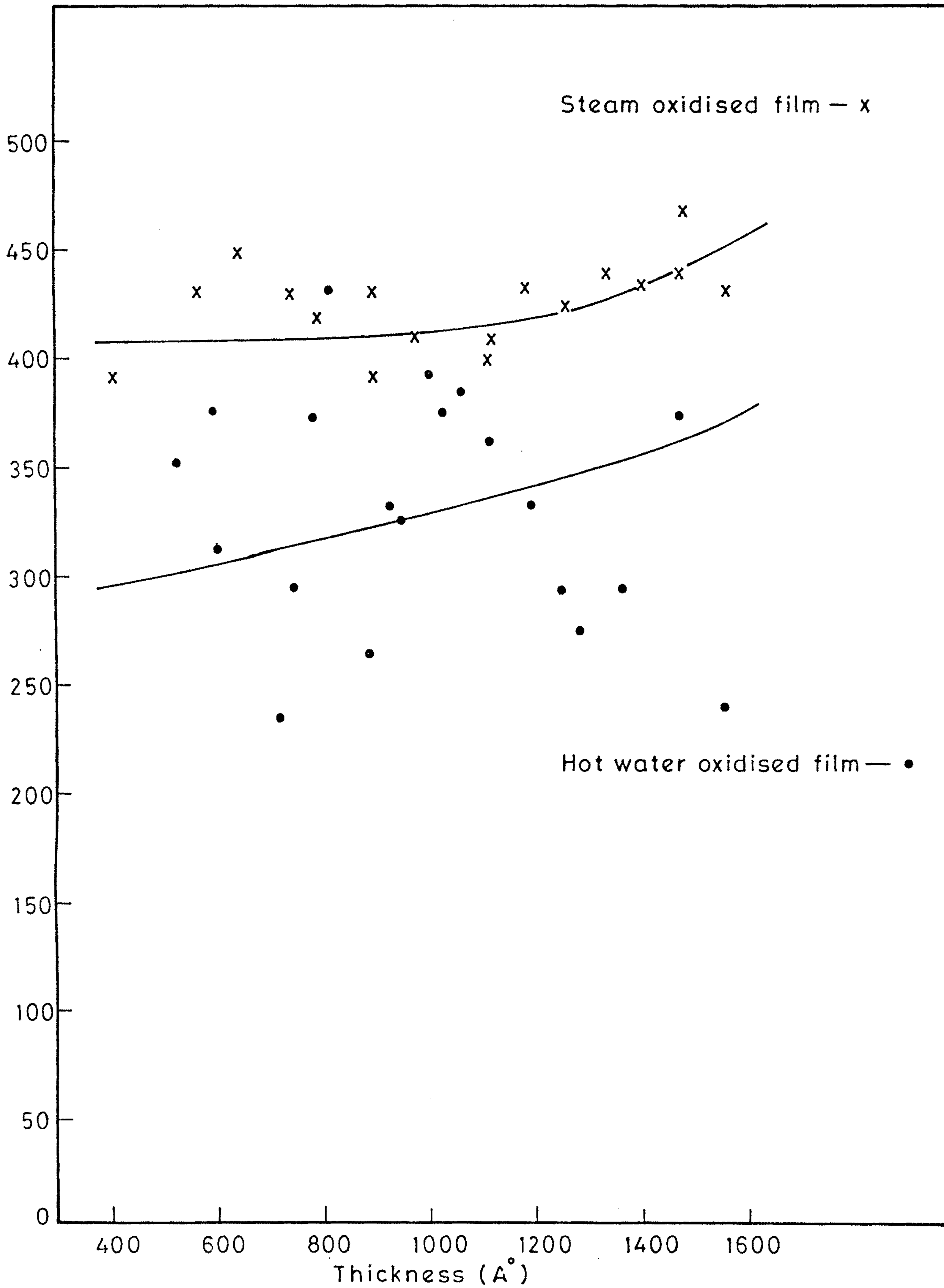

Fig. 3·4·1 – ADHESION OF FRESH Al_2O_3 FILMS FORMED BY STEAM OXIDATION AND HOT WATER OXIDATION.

From the figure it is seen that the adhesion of the films oxidised by steam are very much higher as compared to hot water oxidised films. The adhesion shows randomness in thickness, the randomness being more in hot water oxidised films.

3.4.2 AMBIENT EFFECT ON ADHESION :

Similar to article 3.3.3 here also films were exposed to saturated moisture and heated at 120°C. Sequential exposure experiment as in 3.3.3.2 was not done for adhesion because for every adhesion data the curing time of araldite was 24 hours, which implies that the film will be in the normal atmosphere for 24 hours. so the actual effect of the ambient can not be known. Besides the adhesion measurement by direct pull off method is a destructive method where in the films whose adhesion has been measured can not be used again. So the sequential exposure effects can not be studied on the same film.

3.4.2.1 EFFECT OF SATURATED MOISTURE :

Fig.3.4.2 gives the changes in adhesion as a function of thickness for both steam oxidised and hot water oxidised films, after exposure to saturated moisture (98%) for 3 hours. The adhesion measurement were taken after 24 hours.

It can be seen from this figure that exposure to

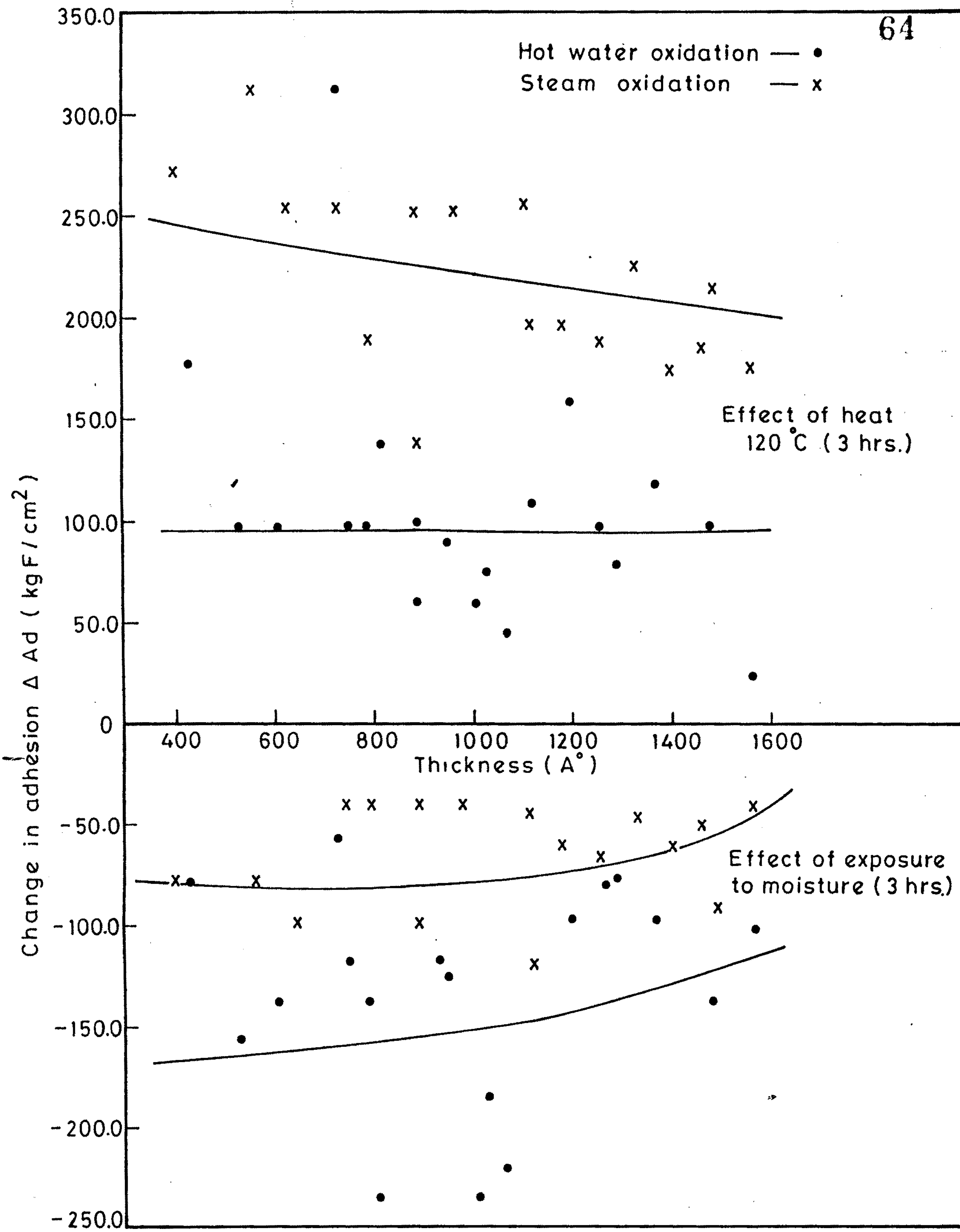

Fig. 3·4·2 – GRAPH OF THICKNESS VERSUS CHANGE IN ADHESION OF STEAM OXIDISED AND HOT WATER OXIDISED Al_2O_3 FILMS.

saturated moisture the adhesion decrease in both the types of films and the decrease is more in hot water oxidised films. The changes in observed adhesion is more than the experimental error which is ± 9.81 KgF/cm^2.

3.4.2.2 EFFECT OF HEAT (120°C) :

Fig.3.4.2 shows the changes in adhesion versus thickness on exposure to heat at 120°C for 3 hours. From the figure it is seen that the exposure to heat has the effect of increasing the adhesion of both types of films. It is also seen that the changes in adhesion of steam oxidised films is higher than hot water oxidised films. Here also the changes in adhesion observed are more than the experimental error.

The post ambient adhesion data of steam oxidised and hot water oxidised films are consolidated in table 3.4 (a) and 3.4 (b).

3.5 D.C. RESISTANCE :

Initially planer resistor was formed on glass substrate and exposed to humid conditions in order to check the sensitivity of films to humidity. It was found that the range of resistance observed for Al_2O_3 films deposited on glass and of plane glass only, was same (of the order of 10^8 ohm), indicating that glass substrate was playing a very dominant role in humidity dependent electrical

Table 3.4(a)

Adhesion (Kg F/cm^2) data of Steam Oxidised Al_2O_3 thin films.

Thickness A°	Fresh film	Saturated moisture film, 3 hr.	Heated film 120°C, 3 hr.
400.0	392.0	313.6	666.4
560.0	431.0	352.8	744.8
636.8	450.0	352.8	705.6
736.8	431.2	392.0	686.0
790.5	420.8	380.1	610.2
890.9	431.2	333.2	570.0
892.2	392.0	352.8	646.8
971.4	411.6	372.4	666.4
1110.1	400.2	356.2	658.2
1120.0	411.6	294.0	608.2
1182.2	431.2	372.4	627.2
1260.0	425.2	360.9	615.1
1333.3	440.2	392.0	666.4
1400.0	435.0	375.8	610.2
1466.0	440.2	390.2	625.8
1487.0	470.4	382.2	686.0
1565.5	431.2	392.0	608.0

Table 3.4(b)

Adhesion (Kg F/cm^2) data of Hot Water Oxidised Al_2O_3 thin films.

Thickness A°	Fresh film	Saturated moisture film, 3 hr.	Heated film 120°C, 3 hr.
433.4	215.6	137.2	392.0
530.9	352.8	196.0	450.8
610.6	313.6	176.4	411.6
725.9	235.0	178.0	548.8
750.1	294.0	176.0	392.0
789.6	372.0	235.0	470.4
816.0	431.0	196.0	568.4
890.9	264.0	166.0	323.4
933.0	332.0	215.0	431.2
950.8	325.0	200.0	415.2
1008.0	392.0	156.0	450.8
1030.0	375.5	190.0	450.8
1070.0	385.0	165.5	430.9
1120.0	362.0	245.0	470.0
1200.0	332.0	235.0	490.0
1265.0	294.0	215.0	392.0
1290.0	274.0	196.0	352.8
1370.0	294.0	196.0	411.6
1480.0	372.4	235.2	470.4
1565.5	240.0	137.2	264.6

behaviour of films. So it was found necessary to use a better water repellent substrate. Polycrystalline Al_2O_3 substrate (Kyocera Japan) of purity 99.6% and good surface smoothness was used as a substrate. It has a volume resistivity of $>10^{14}$ ohm cm (Kyocera Design Guide Catlogue). and is also water repellant.

All the data which will be reported on D.C. resistance is of films deposited on Al_2O_3 substrates, though the refractive index and adhesion studies are done on glass substrates where the glass characteristics does not interfere with the film characteristics.

All the D.C. resistance experiments were performed on films of average thickness 700 A°, 1000 A°, 1300 A° for steam oxidised case and average thickness of 1000 A°, 1300 A° for hot water oxidised films. Each curve is an average of 3-4 samples with the thickness range ± 50 A°. All the figures in the article 3.5 are the log - linear plots.

3.5.1 I-V CHARACTERISTICS :

Fig. 3.5.1 shows the I-V charactristics of steam oxidised and hot water oxidised Al_2O_3 films. It is seen that the change of current with voltage has a exponential rise. The changes- being more for steam oxidised films as compared to hot water oxidised films. All the films upto around 3V obeys ohms law. For steam oxidised films higher thickness

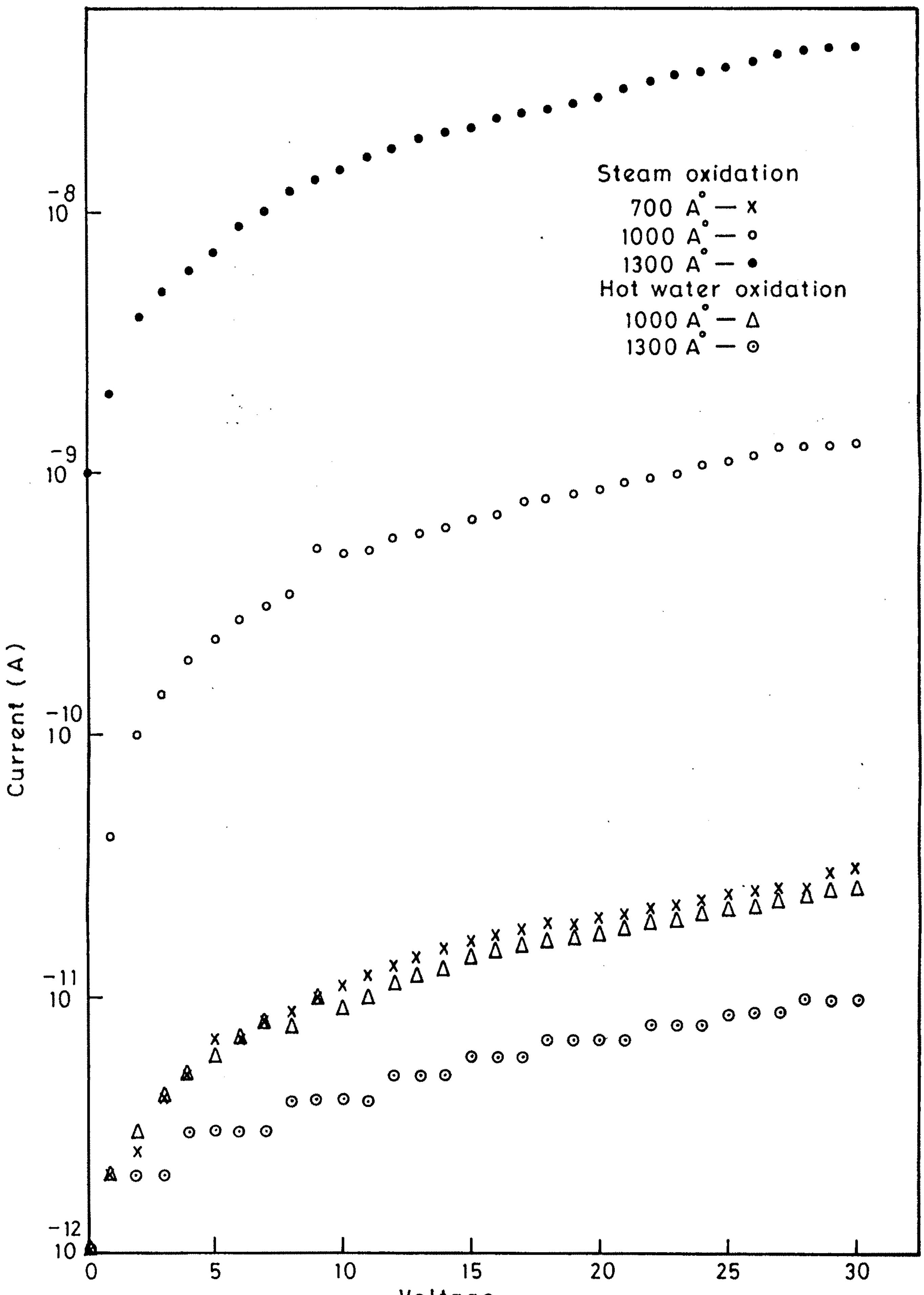

Fig.3·5·1 — I-V CHARACTERISTICS OF Al_2O_3 FILMS FORMED BY STEAM OXIDATION AND HOT WATER OXIDATION OF ALUMINIUM.

films shows higher current values where as for hot water oxidised films current increases for lower thickness films.

3.5.2 AMBIENT EFFECT ON D.C. RESISTANCE :

3.5.2.1 EFFECT OF SATURATED MOISTURE :

The resistance versus time of exposure to humidity is depicted in Fig.3.5.2.1.

The films were kept in 98% humidity. the response of the film was monitored for 180 minutes and the current measured after every one minute. The films were then exposed to atmosphere by removing the lid of the humidity chamber and the film response was measured for 2 minutes in air, the reading taken after every 5 seconds.

From the figure it is seen that in general hot water oxidised films have a higher resistance as compared to steam oxidised film. The thinner steam oxidised films show higher resistance as compared to thicker films where as for hot water oxidised film thicker films show higher resistance as compared to thinner films.

It is seen that within 1 minute of exposure to moisture there is a steep decrease in resistance as seen in the figure. After one minute the fall in resistance continues though not steeply till about 20-25 minutes, and a tendency to reach equilibrium state after around 30 minutes. Till 180 minutes there is a very slight tendency of decrease

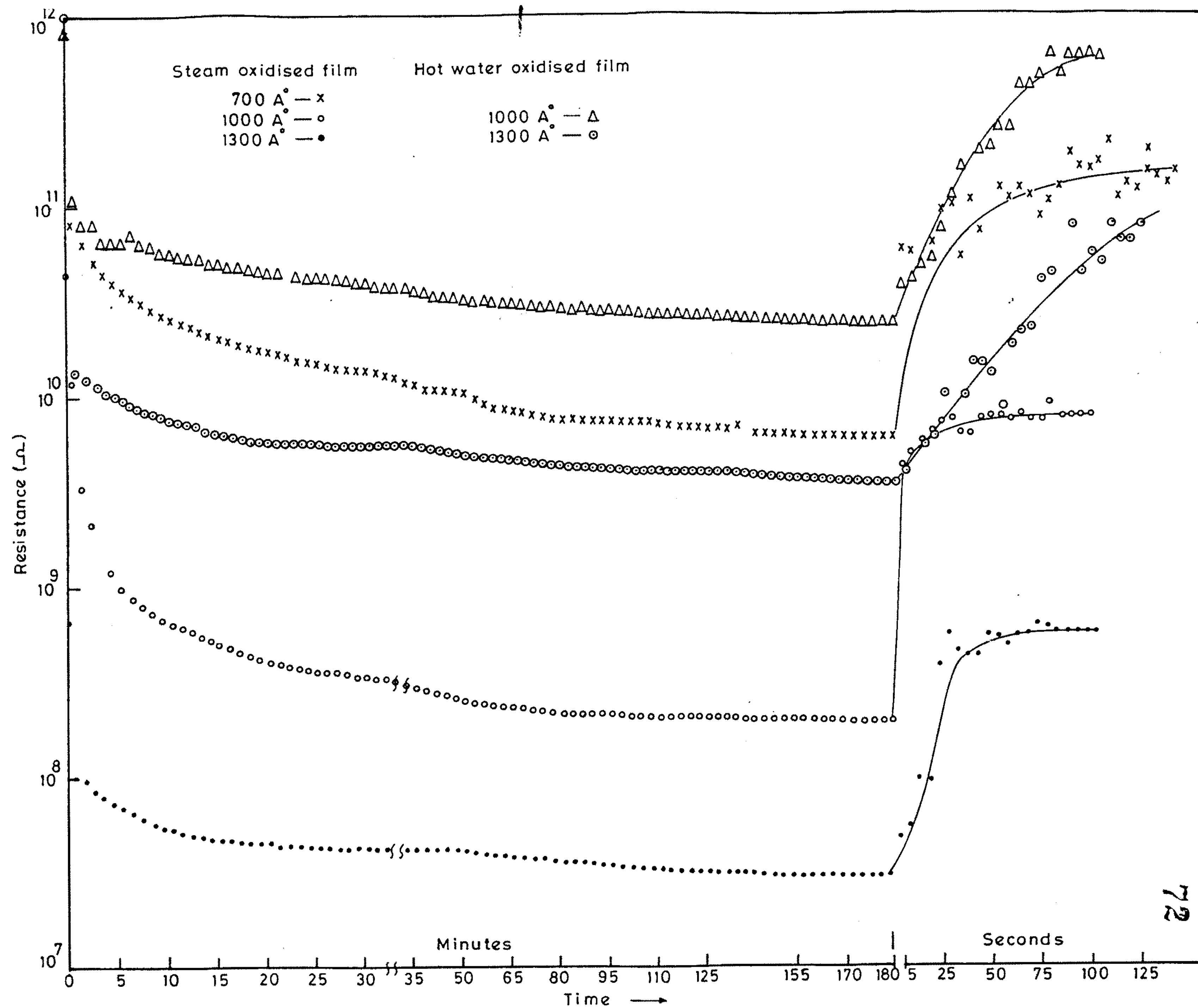

Fig. 3·5·2·1 – RESISTANCE VERSUS TIME OF Al_2O_3 FILMS ON EXPOSURE TO 3 HR. MOISTURE FORMED BY STEAM OXIDATION AND HOT WATER OXIDATION.

of resistance. Within the first 5 minutes the rate of decrease of resistance is highest in hot water oxidised films of 1300 A°. On exposure to air there is a rapid increase in resistance with 5 second and this rise continues till about 50 second for steam oxidised films and about 100 second for hot water oxidised films after which a tendency for equilibrium is reached. The values of resistance of fresh film and after 1 minutes, 5 minutes, 30 minutes, 60 minutes, 180 minutes in moisture and further resistance after 5, 50 and 100 seconds in air are given in table.3.5.2.1 .

3.5.2.2 VARIATION WITH RELATIVE HUMIDITY :

Fig. 3.5.2.2 shows the change of resistance with relative humidity. The films are seen to be sensitive to changes in relative humidity with a resistance change of 2 orders of magnitude for steam oxidised films of 1000 A° and 700 A° thickness and 1 order change in hot water oxidised films of 1300 A° and 1000 A°.The steam oxidised films of 1300 A° shows comparatively lesser changes in resistance with change in humidity levels.

3.5.2.3 MOISTURE - HEAT - AIR CYCLE :

The moisture heat air cycle was as follows. After measuring the fresh film resistance the films were kept in 98% moisture for 30 minutes. The resistance values measured after every 5 minutes. Then the films were heated to 40°C

Table 3.5.2.1

D.C. Resistance Of Al_2O_3 Films On Exposure To Saturated Moisture And Air

Time	Steam Oxidation			Hot water Oxidation	
	700 Å	1000 Å	1300 Å	1000 Å	1300 Å
Fresh	$8.0*10^{11}$	$4.44*10^{10}$	$6.6*10^{8}$	$8.0*10^{11}$	$1.3*10^{12}$
Time after moisture exposure					
1 minute	$8.0*10^{10}$	$1.2*10^{10}$	$1.0*10^{8}$	$1.0*10^{11}$	$1.3*10^{10}$
5 minute	$4.08*10^{10}$	$1.2*10^{9}$	$7.5*10^{7}$	$6.6*10^{10}$	$1.0*10^{10}$
30 minute	$1.32*10^{10}$	$3.4*10^{9}$	$4.28*10^{7}$	$4.04*10^{10}$	$5.63*10^{9}$
60 minute	$9.32*10^{9}$	$2.42*10^{8}$	$3.96*10^{7}$	$3.22*10^{10}$	$4.63*10^{9}$
180 minute	$6.22*10^{9}$	$2.00*10^{8}$	$3.12*10^{7}$	$2.53*10^{10}$	$3.47*10^{9}$
Time after expose to air					
5 second	$6.06*10^{10}$	$4.4*10^{9}$	$4.25*10^{7}$	$2.53*10^{10}$	$3.47*10^{9}$
50 second	$2.10*10^{11}$	$8.0*10^{9}$	$4.5*10^{8}$	$2.0*10^{11}$	$1.42*10^{10}$
100 second	$1.53*10^{11}$	$8.0*10^{9}$	$6.0*10^{8}$	$6.6*10^{11}$	$5.7*10^{10}$

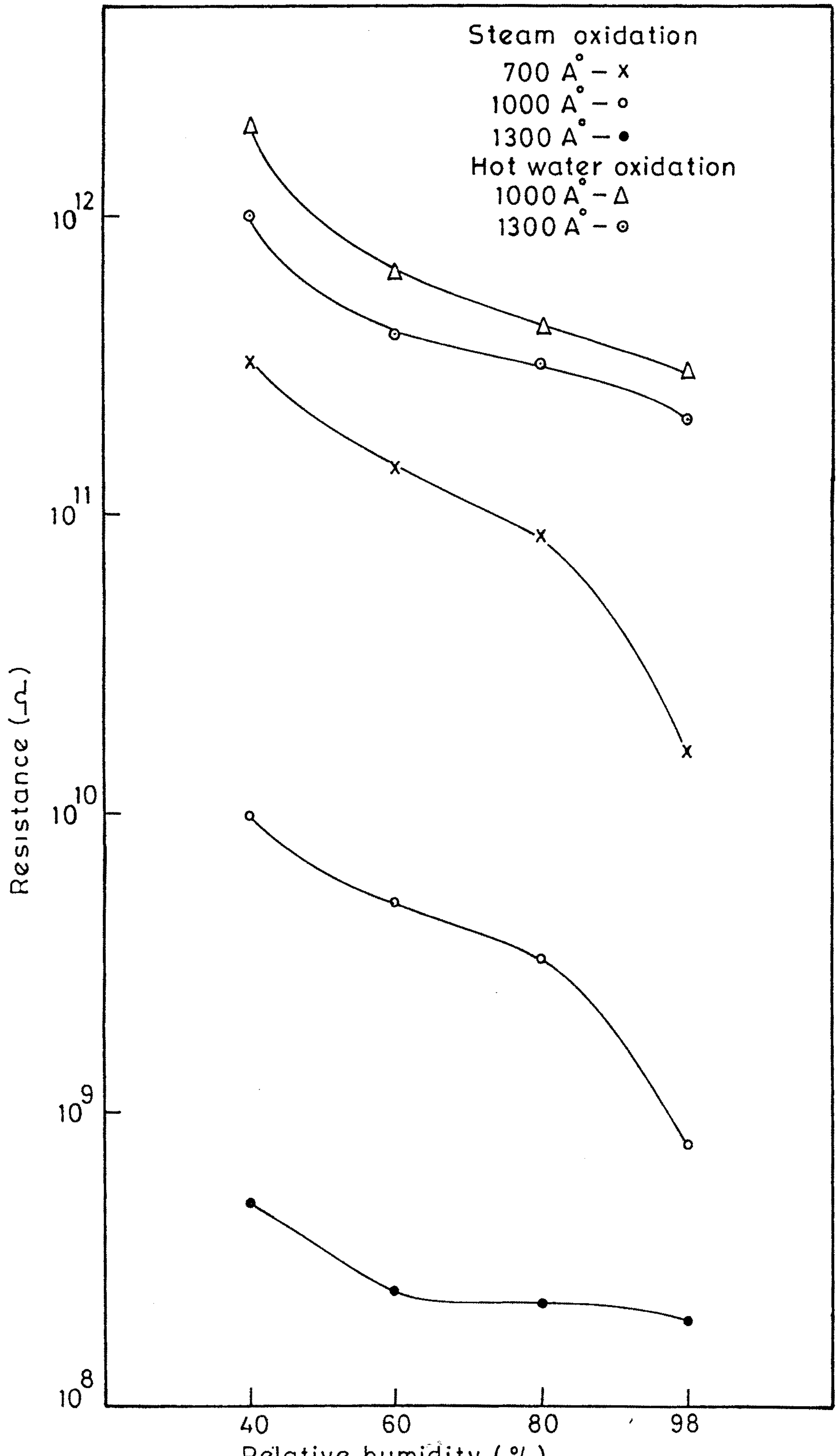

Fig. 3·5·2·2 – RESISTANCE VERSUS RELATIVE HUMIDITY OF Al_2O_3 FILMS FORMED BY STEAM OXIDATION AND HOT WATER OXIDATION OF ALUMINIUM.

for 30 minutes, the resistance values measured after every 5 minutes. The films were then exposed to room temperature and resistance values measured. Again it was kept in moisture and the cycle repeated 3 times. this experiment was performed for two thicknesses i.e. 1300 A° and 1000 A°. Fig.3.5.2.3 shows the graph of steam oxidised films. For hot water oxidised films the current reading after heating went beyond the range of the picoammeter used. So the resistance data for the heating part of the cycle could not be measured hence could not be reported.

As expected, on exposure to moisture there is a decrease in resistance and on heating there is increase in resistance. On exposure to room temperature the resistance decreases again, though not to the same extent as decrease in moisture.This decrease and increase trend is repeated on repeating the cycle. The changes in the 1^{st} heating cycle of 1300 A° thick films are more as compared to other cycles.

3.5.2.4 EXPOSURE TO 98% HUMIDITY - AIR CYCLING :

From the experiment of continous exposure of films to 98% humidity upto 180 minutes it was observed that films have a tendency to attain saturation after about 20 minutes (article 3.5.2.1). So in this moisture - air cycling observations of variation of resistance the time period of moisture exposure was kept up to 25 minutes. Fig 3.5.2.4

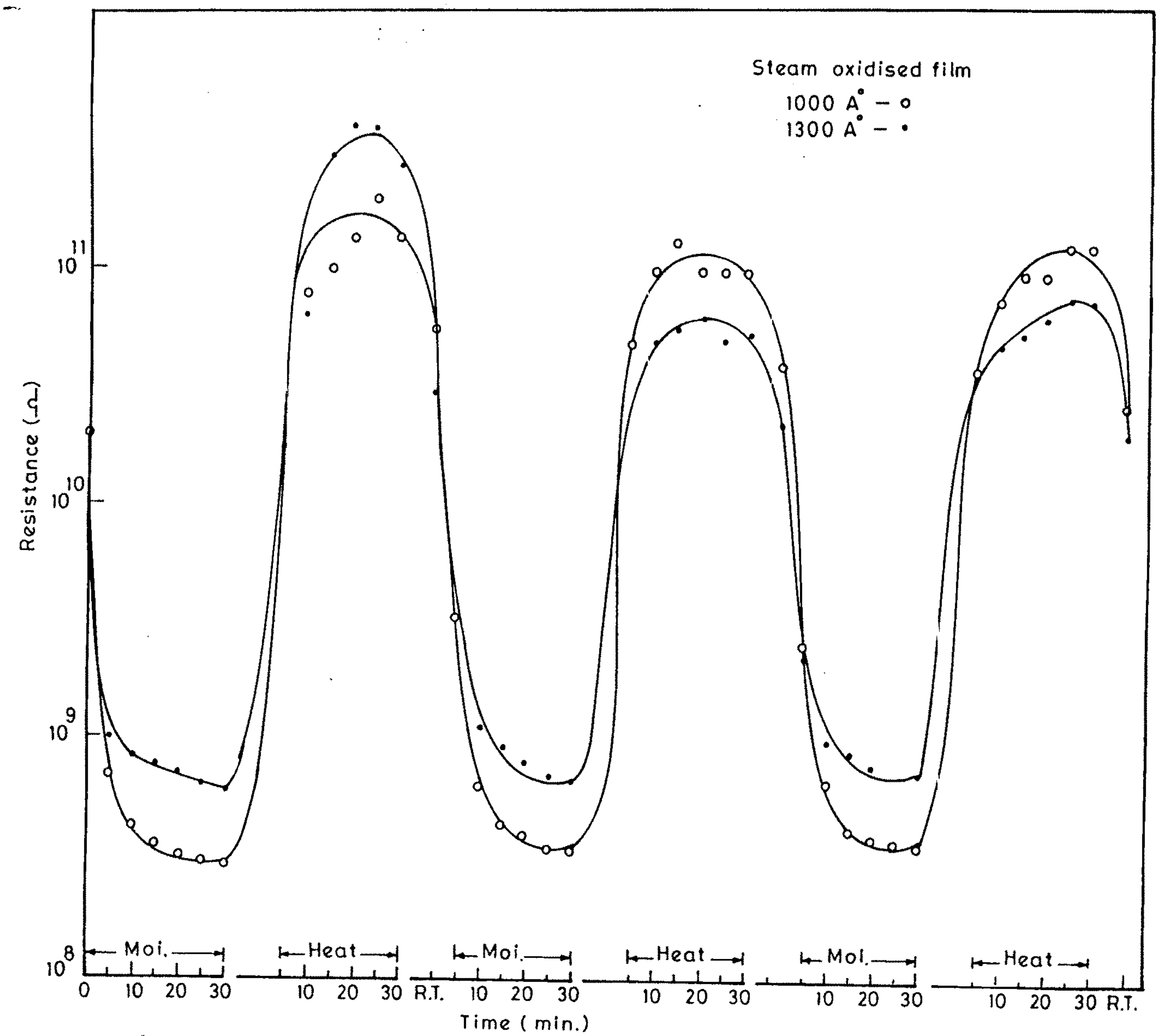

Fig. 3·5·2·3 – RESISTANCE OF Al_2O_3 FILMS ON EXPOSURE TO MOISTURE AND HEAT FORMED BY STEAM OXIDATION OF ALUMINIUM.

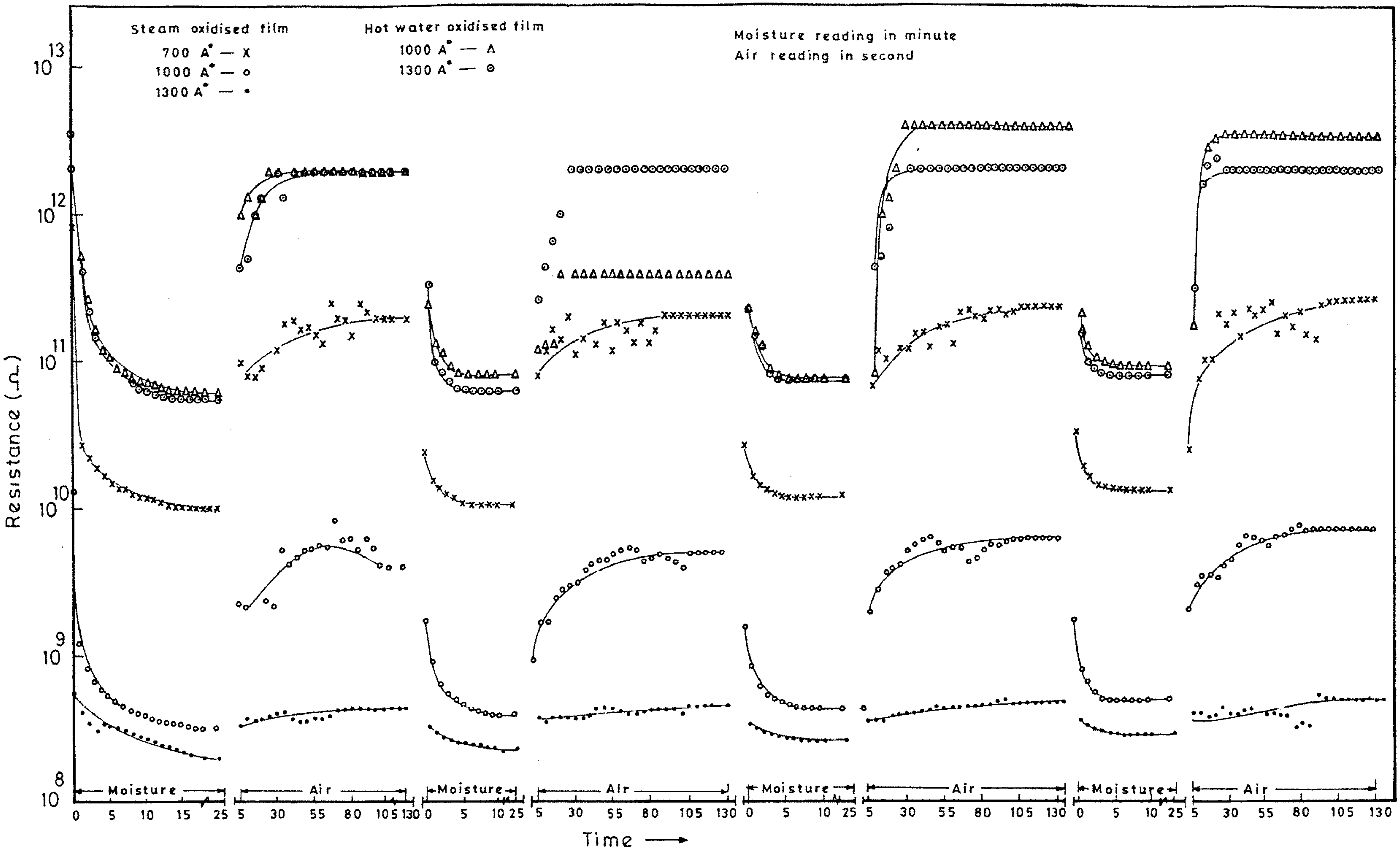

Fig. 3·5·2·4 – RESISTANCE OF Al_2O_3 FILMS EXPOSED TO 98% SATURATED MOISTURE AND AIR FORMED BY STEAM OXIDATION AND HOT WATER OXIDATION.

shows the graph of resistance versus time of moisture - air exposure cycling. Four such cycles were performed.

It is seen that similar to fig 3.5.2.1 the resistance decreases on exposure to moisture and increases on exposure to air. The equilibrium value in air does not reach the fresh film value. Repeated cycling does not show any change in the decrease increase behaviour pattern.It is seen that the time to attain of eqilibrium in humidity decreases after successive cycling. For 1st cycle it takes 15-25 minutes, 2nd cycle 10-15 minutes, 3rd cycle 5-10 minutes, and 4th cycle 4-7 minutes. The hot water oxidised Al_2O_3 films attaining equilibrium faster than steam oxidised films. On exposure to air equilibrium is attained within about 30 second for all the cycles.

3.6 IR AND XRD STUDIES :

3.6.1 IR STUDIES :

As already mentioned in article 2.10 the IR spectrum was taken on glass substrate and the effect of moisture on IR spectrum of Al_2O_3 observed. In order to see the behaviour of substrate on IR region of plain glass substrate and plain glass exposed to moisture for 3 hrs and heated to 40^{o}C for 1 hour are plotted in fig 3.6.1. From fig. it is seen that on exposure to moisture there is increase in transmittance from 3500 to 2500 cm^{-1} and on

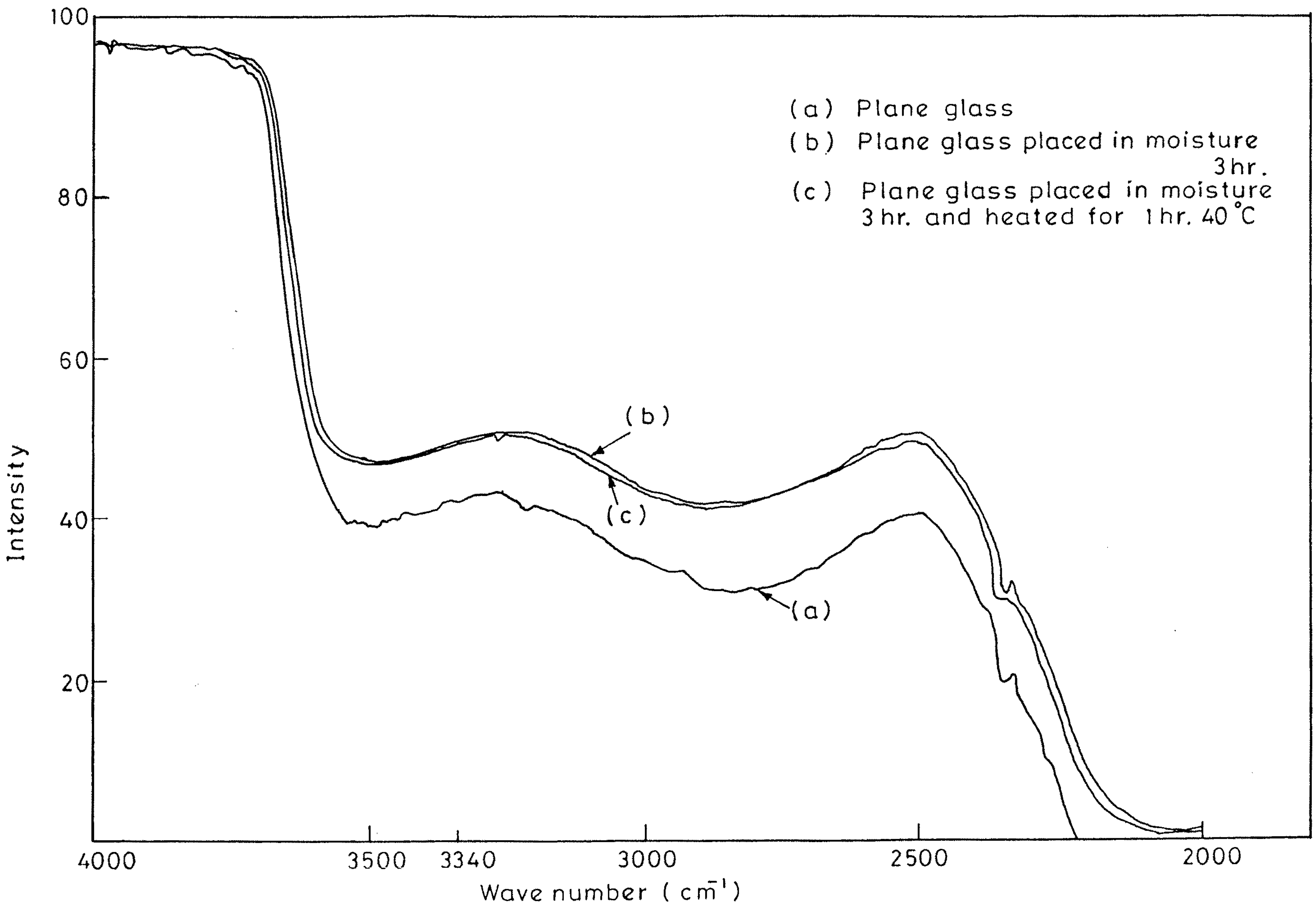

Fig. 3·6·1 — IR Spectra of plane glass substrate .

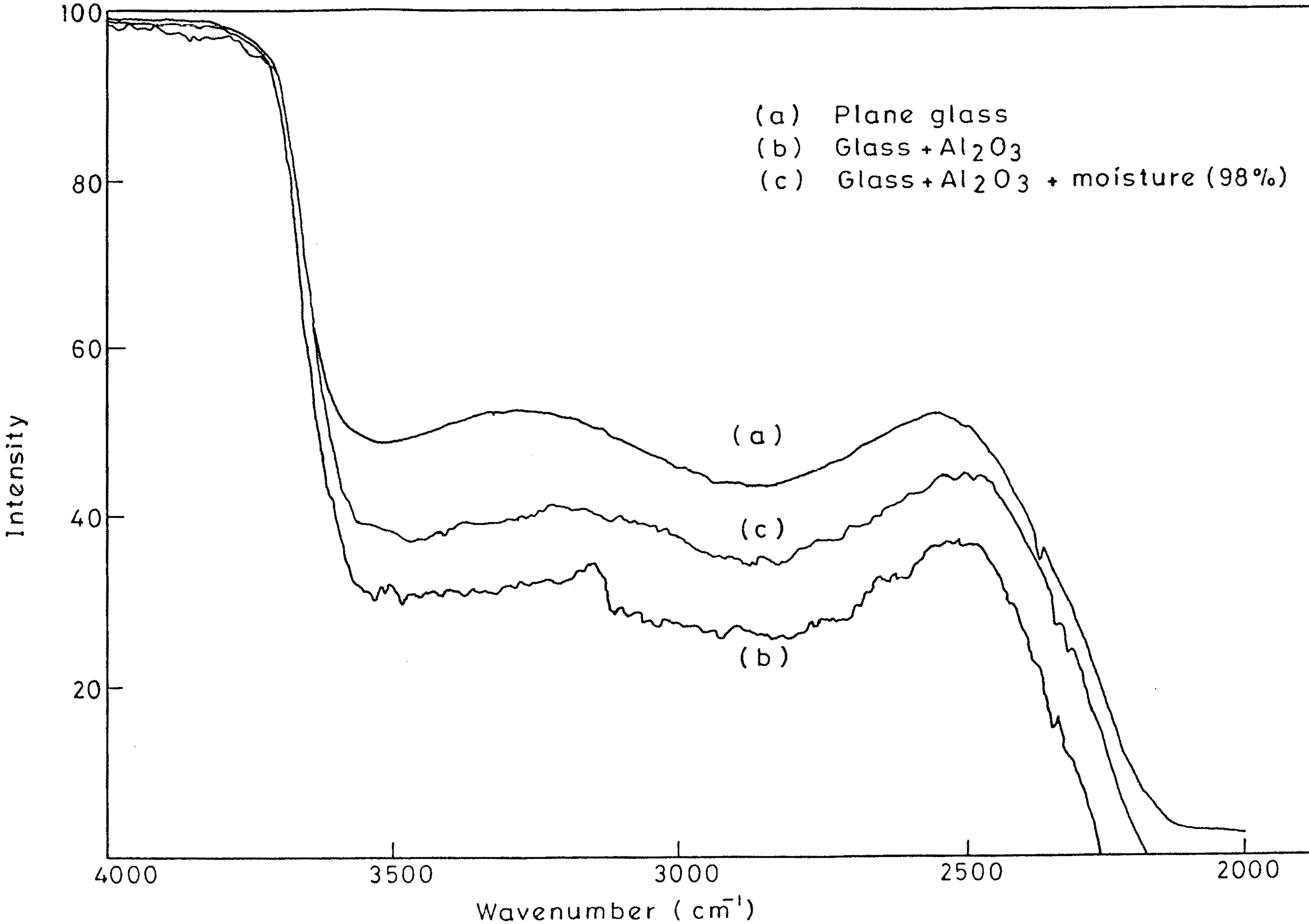

Fig. 3·6·1 (a) IR SPECTRUM OF THIN FILM Al_2O_3 FORMED BY STEAM OXIDATION.

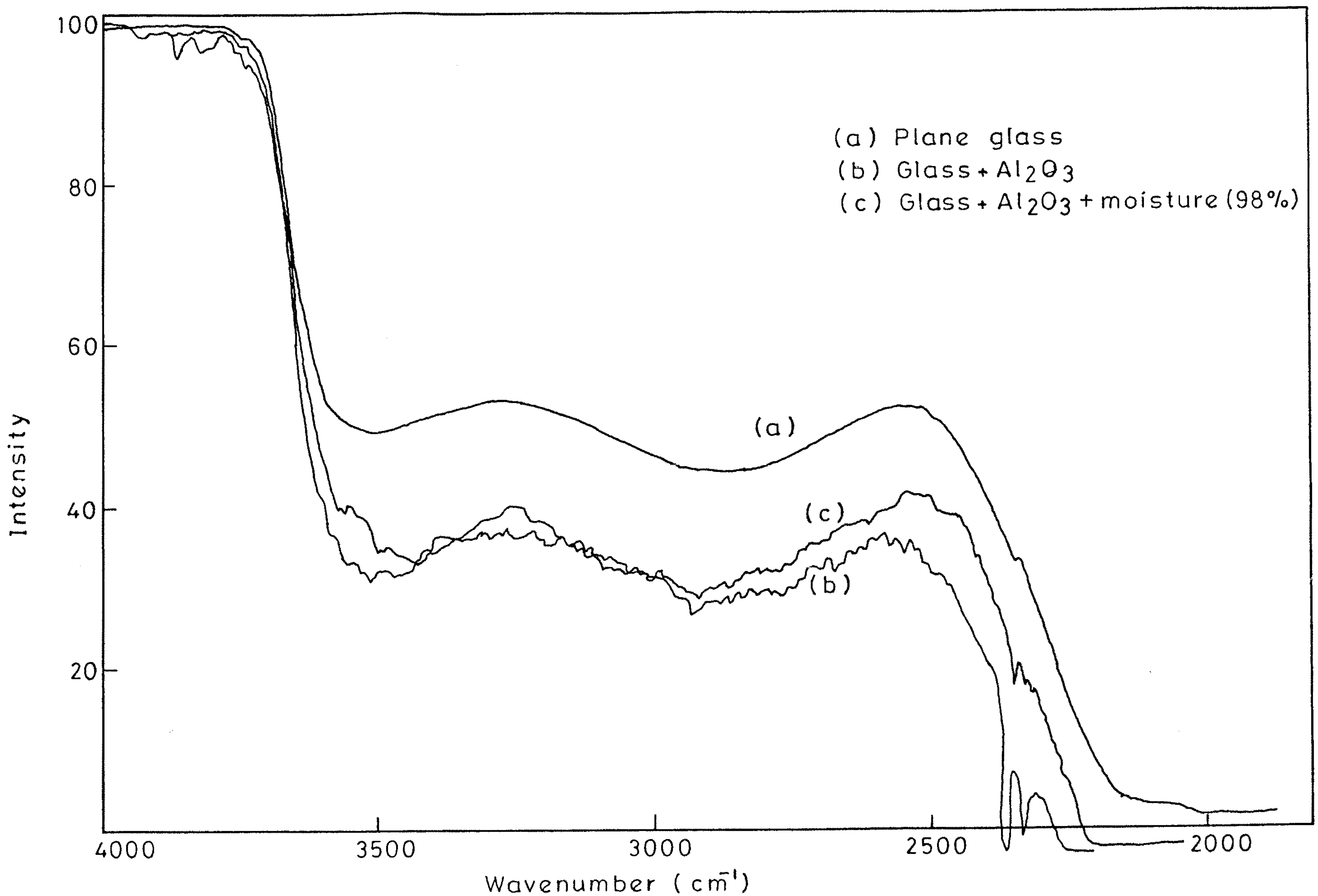

Fig. 3·6·1 (b) – IR SPECTRUM OF THIN FILM Al_2O_3 FORMED BY HOT WATER OXIDATION.

heating to 40°C there is no change in transmittance from the moisture exposed values.

Fig.3.6.1.(a), 3.6.1.(b) gives the IR plots of steam oxidised and hot water oxidised Al_2O_3 films respectively. It is seen that Al_2O_3 films show lesser transmittance than plain glass. Both steam oxidised and hot water oxidised films show almost same transmittance values in the range studied. On exposure to moisture there is increase in transmittance for steam oxidised films but it does not attain the plain glass value. Where as in hot water oxidised films (i.e.in fig.3.6.1.(b)) between 3500-3000 cm^{-1} there is a slight decrease in transmittance, the changes being lesser than those obtained in steam oxidised films.

3.6.2 <u>XRD STUDIES</u> :

Fig.3.6.2(a) and 3.6.2(b) shows the XRD plots of steam oxidised and hot water oxidised films of Al_2O_3 respectively. The d–values and identification of planes is given in table 3.6.2.

From the plots and table it is seen that the weak crystalline order with a predominance of α-phase in steam oxidised Al_2O_3 films and δ-phase in hot water oxidised Al_2O_3 films are present.

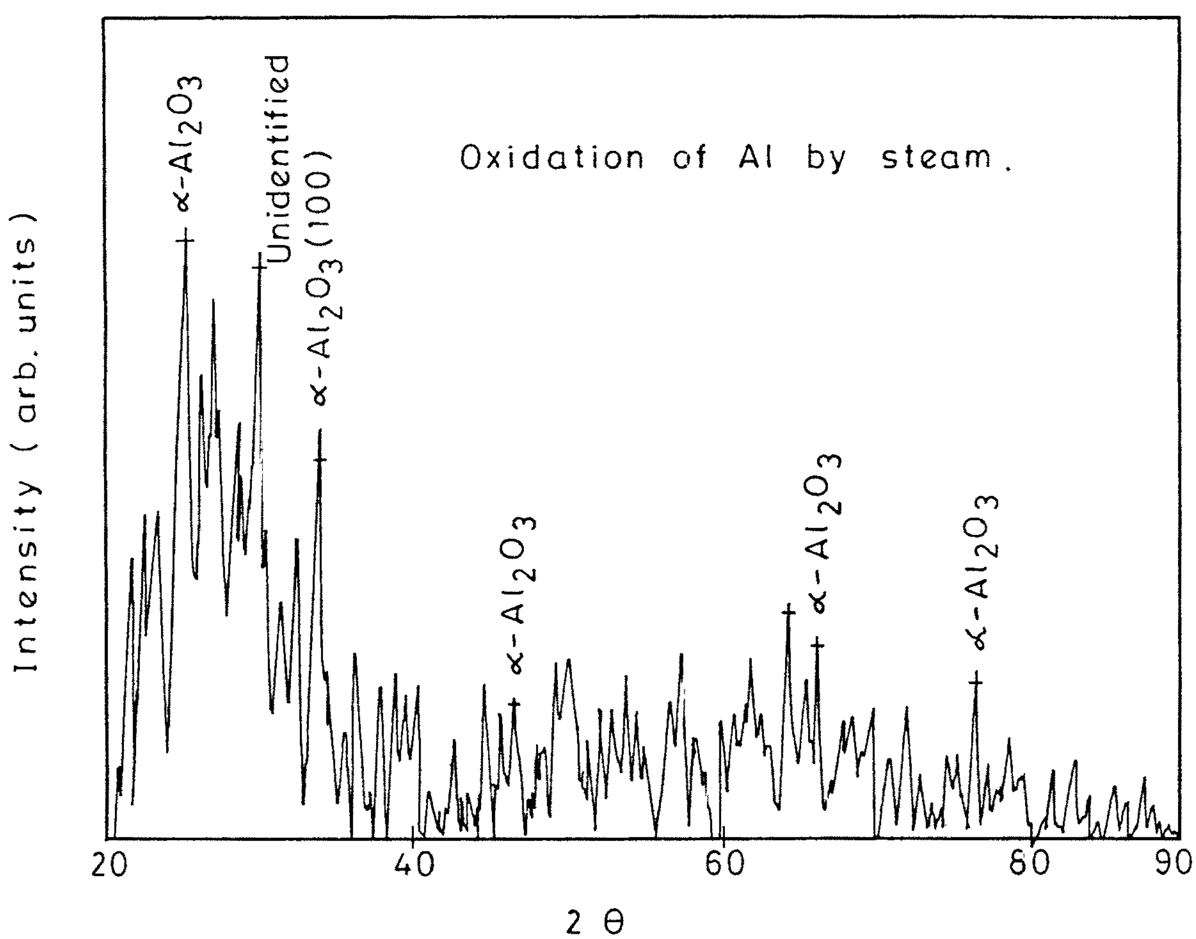

Fig. 3·6·2 (a) — XRD PLOT OF Al_2O_3 FILMS FORMED BY STEAM OXIDATION.

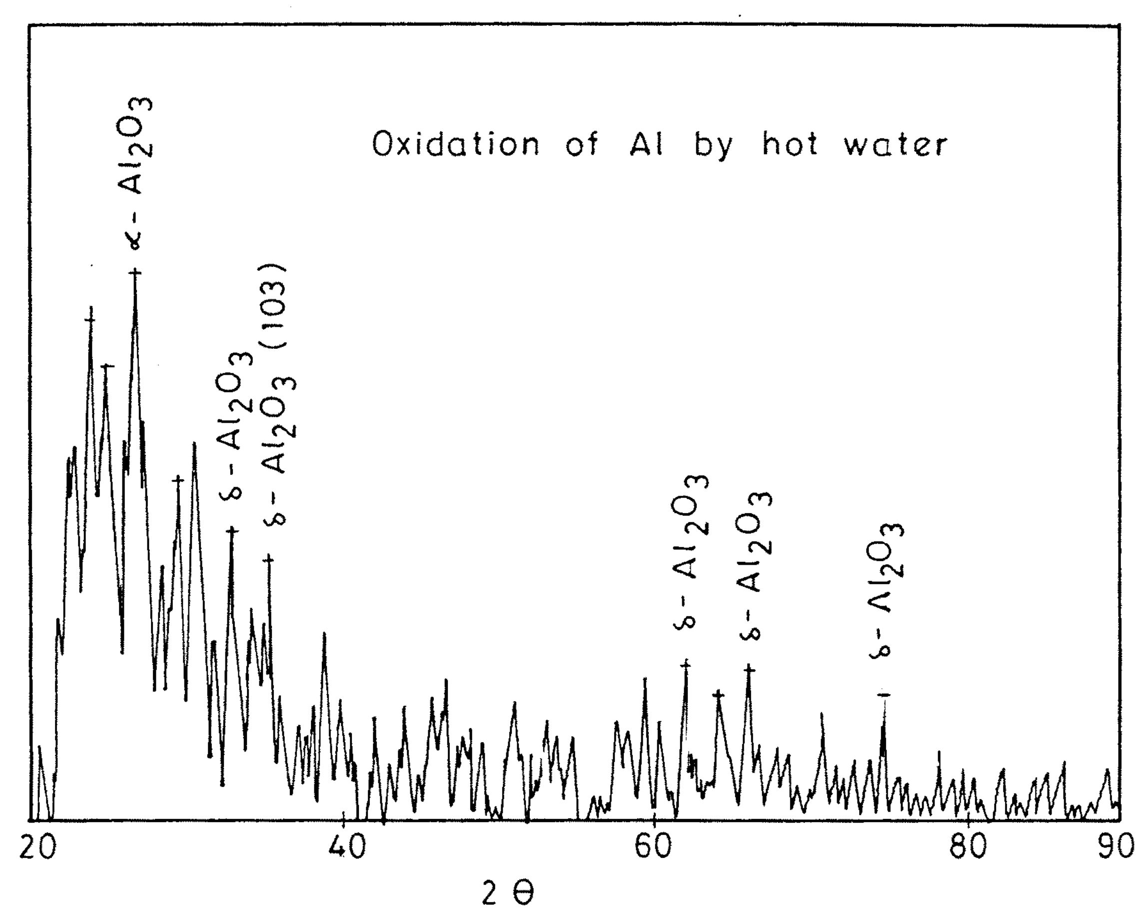

Fig. 3·6·2 (b) — XRD PLOT OF Al_2O_3 FILMS FORMED BY HOT WATER OXIDATION.

Table 3.6.2

X-ray diffraction data of steam oxidised Al_2O_3 thin film
Thickness 1C00 A°

2 θ	d	I/Io	Remarks
25.960	3.429	93	α–Al_2O_3 (012)
29.22	3.054	100	Unidentified
32.18	2.779	71	Unidentified
37.44	2.400	43	α–Al_2O_3 (100)
46.46	1.953	39	α–Al_2O_3 (001)
48.50	1.875	40	α–Al_2O_3 (203)
50.66	1.800	38	α–Al_2O_3 (015)
56.200	1.635	30	Al_2O_3 (204)
66.460	1.406	24	α–Al_2O_3 (124)
76.76	1.243	26	α–Al_2O_3

X ray diffraction data of hot water oxidised Al_2O_3 thin film
Thickness 1000 A°

2 θ	d	I/Io	Remarks
26.62	3.34	100	Unidentified
29.60	3.01	100	Unidentified
32.99	2.717	89	δ-Al_2O_3
35.180	2.549	47	δ-Al_2O_3 (103)
44.520	2.033	52	δ-Al_2O_3
66.06	1.413	27	δ-Al_2O_3
62.140	1.493	27	δ-Al_2O_3
64.220	1.449	23	δ-Al_2O_3
74.820	1.268	23	δ-Al_2O_3

3.7 SUMMARY OF SOME IMPORTANT RESULTS :

1) The refractive index of steam oxidised films are higher than hot water oxidised Al_2O_3 films.
2) The adhesion of steam oxidised films are very much higher than hot water oxidised Al_2O_3 films.
3) The steam oxidised films grows faster as compared to hot water oxidised Al_2O_3 films.
4) The porosity of hot water oxidised films are slightly higher than steam oxidised Al_2O_3 films.
5) The refractive index is not thickness dependent.
6) The hot water oxidised films shows higher D.C. resistance as compared to steam oxidised Al_2O_3 films.
7) Both films are sensitive to humidity ambients.
8) On exposure to 98% humidity, the refractive index decreases, adhesion decreases and D.C. resistance also decreases.
9) IR data shows absorption band 2500 cm^{-1} to 3500 cm^{-1}.
10) XRD results indicate a more amorphous like crystal structure.
11) Heating to 120°C, decrease in refractive index, increase in adhsion.
12) Sequencial moisture - heat (40°C) exposure shows changes in properties.