CHAPTER - III

RESULTS

Aging studies of single films of cerium oxide films : non-chopped and chopped under different ambient conditions.

3.1 INTRODUCTION.

From the optical technology point of view thin films of cerium oxide are very important because of their extensive use as high refractive index material in various optical coatings. The study of adhesion, stress and (Δ) (Ψ) for various thickness range and the study of the aging of these films under various ambients usually encountered during usage, would help in improving these coatings to withstand the environmental effects.

In this work the adhesion tester (Direct Pull Off method), stress measurement set up (interferometric technique) and ellipsometric technique were used to determine adhesion, stress and (Δ) , (Ψ) values respectively of the films. The chapter is divided into various subsections depending on the ambients used.

3.2 GENERAL PLAN IN THE PRESENT WORK.

The present work is concerned with the study of aging due to various ambients, and measurement of adhesion and stress of cerium oxide films and the effect of chopping on its properties. The films of cerium oxide were prepared as given in chapter II. The experiments were carried out with a view to know as far as possible the effect of chopping and the aging process operative in these films under various ambients and possible means of reducing it. These films were studied over a thickness range, 400 Å to 2800 Å. For the sake of convenience the thickness has been divided into four different ranges.

1) 400 - 1000 Å.
2) 1000 -1600 Å.
3) 1600 - 2200 Å.
4) 2200 - 2800 Å.

Thicknesses were found by Fizeau fringe method.

The basic measurement of interest was adhesion, stress and (Δ), (Ψ) values under different ambient conditions of

1) Air at room temperature.
2) Effect of room temperature moisture.
3) Effect of cold moisture.
4) Effect of salty moisture.
5) Effect of heat.

In all the cases the observation medium was air and the initial readings were taken immediately after exposure to air from the vacuum system with about 3 to 5 minutes time for each sample.

For adhesion since the curing time of araldite was about 24 hours, the adhesion measurements were done only after 24 hours after removal from vacuum.

For adhesion and stress measurement the samples were used as it is. For locating the exact spot for repeated observations, for ellipsometer, the initial observation spot was marked on the back side of the substrate. The marking did not affect the null position.

The parameters measured were,

a) Adhesion - spring balance reading at the time of breakage of bonding.

b) Stress - Changes in traveling microscope - reading for diameter determination.

c) Ellipsometer - The polarizer angle P and analyzer angle A, from these P and A values, the phase difference (Δ) and amplitude attenuation ratio (Ψ) were found out using equations, 1.6.1.16 and 1.6.1.17.

3.3 DATA OF ADHESION AND ELLIPSOMETRIC MEASUREMENT OF FRESH FILM.

3.3.1 SCATTER DIAGRAM

Figure 3.3.1 (1) and 3.3.1 (2) gives the scatter diag. of adhesion and (Δ) and (Ψ) respectively as a function of thickness for nonchopped and chopped, cerium oxide films.

All the available experimental data of fresh films are plotted in this graph.

Since the samples for stress measurement were not many in number, scatter diagram was not plotted.

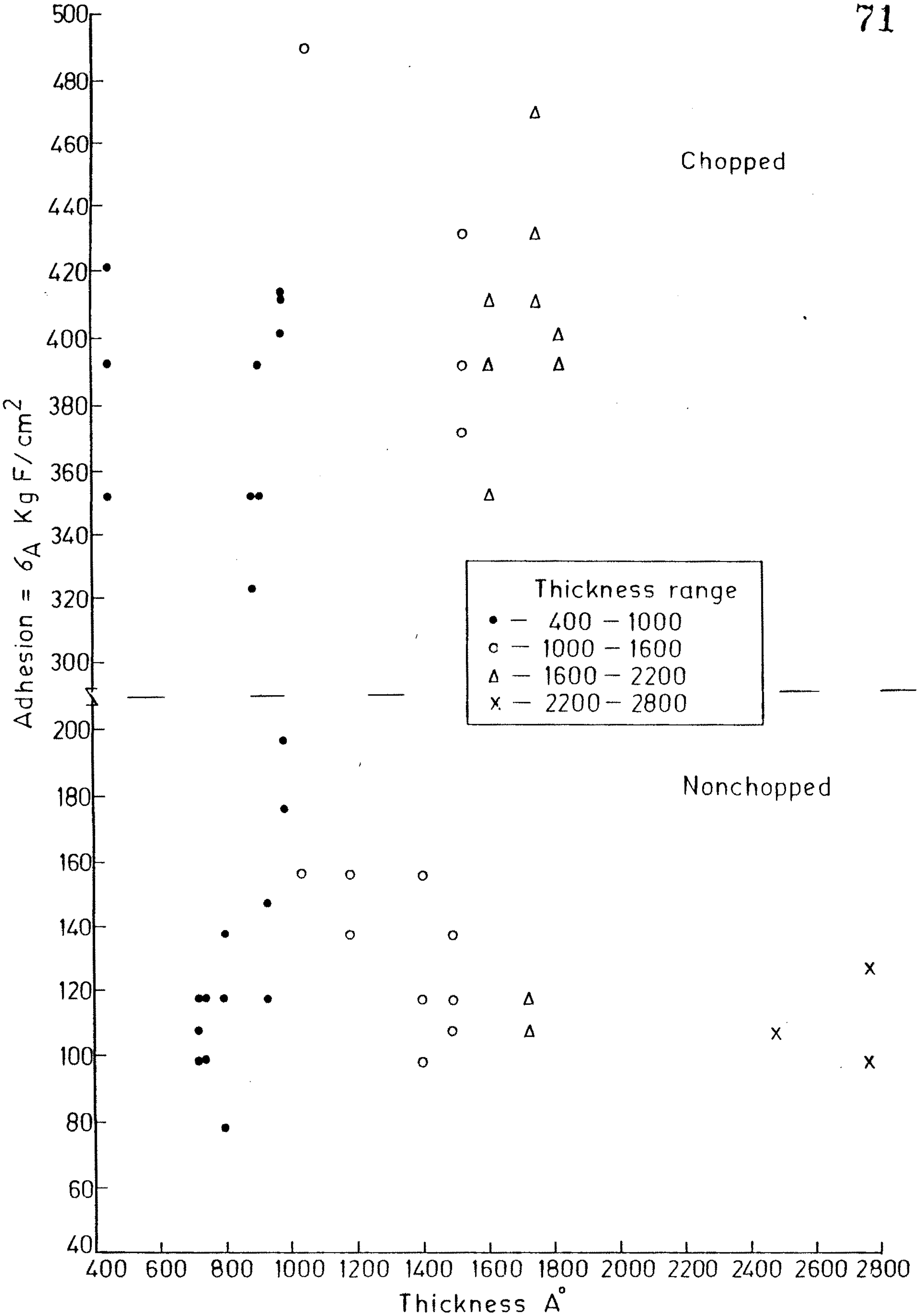

Fig. 3·3·1 (1) - Scatter diagram of adhesion vs thickness for nonchopped and chopped films.

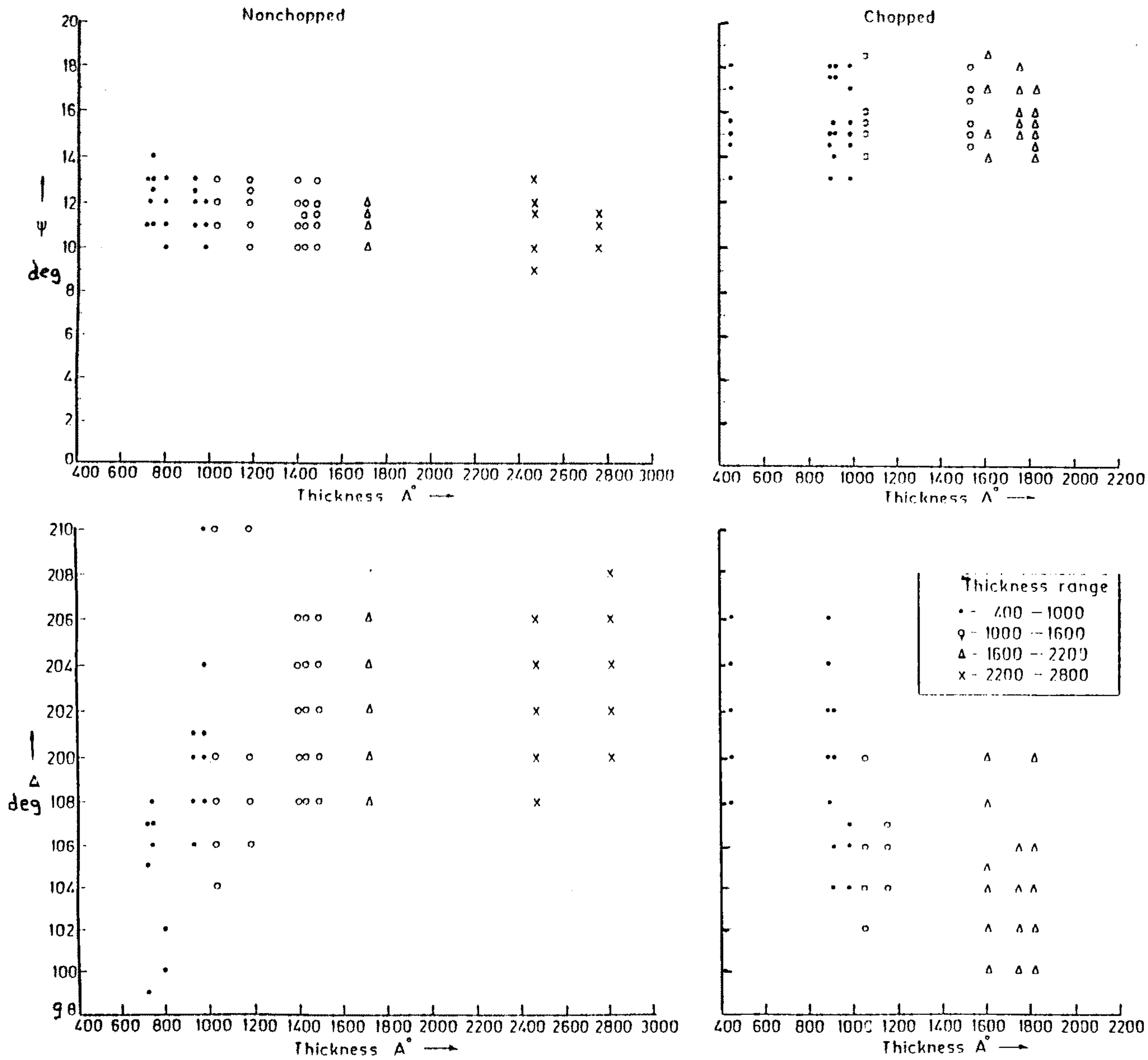

Fig. 3·3·1 (2) – Scatter diagram of Δ, ψ vs thickness, for nonchopped and chopped films.

From fig.3.3.1 (1) it is given that for all the thicknesses from 400-2800 Å the adhesion of chopped films are more than double that of nonchopped films.

Around 1000 Å thickness there is sharp increase in adhesion for both nonchopped and chopped films.

Though there is not much thickness dependency of nonchopped films, the chopped films shows slightly higher adhesion for higher thickness (~ 1600 Å).

From fig. 3.3.1 (2) it is seen that (Δ) increases as thickness increases for nonchopped films, where as for chopped films (Δ) decreases as thickness increases. (Ψ) for nonchopped cerium oxide films is lesser than (Ψ) for chopped films, there is not much thickness dependency for either nonchopped or chopped films. The scatter in chopped films is slightly higher than that of non chopped films.

The error in measurement of (Δ) and (Ψ), on the average it is about 1°, with very careful experimentation 0.6 to 0.8° accuracy can be obtained.

3.3.2 AVERAGE DATA FOR FRESH FILMS

The average values of adhesion, stress, (Δ) and (Ψ) are given in fig. 3.3.2 (1),(2),(3).

From fig.3.3.2 (1) it is seen that for nonchopped films in thickness range 1000-1500 Å there is increase in adhesion as compared to other thicknesses.

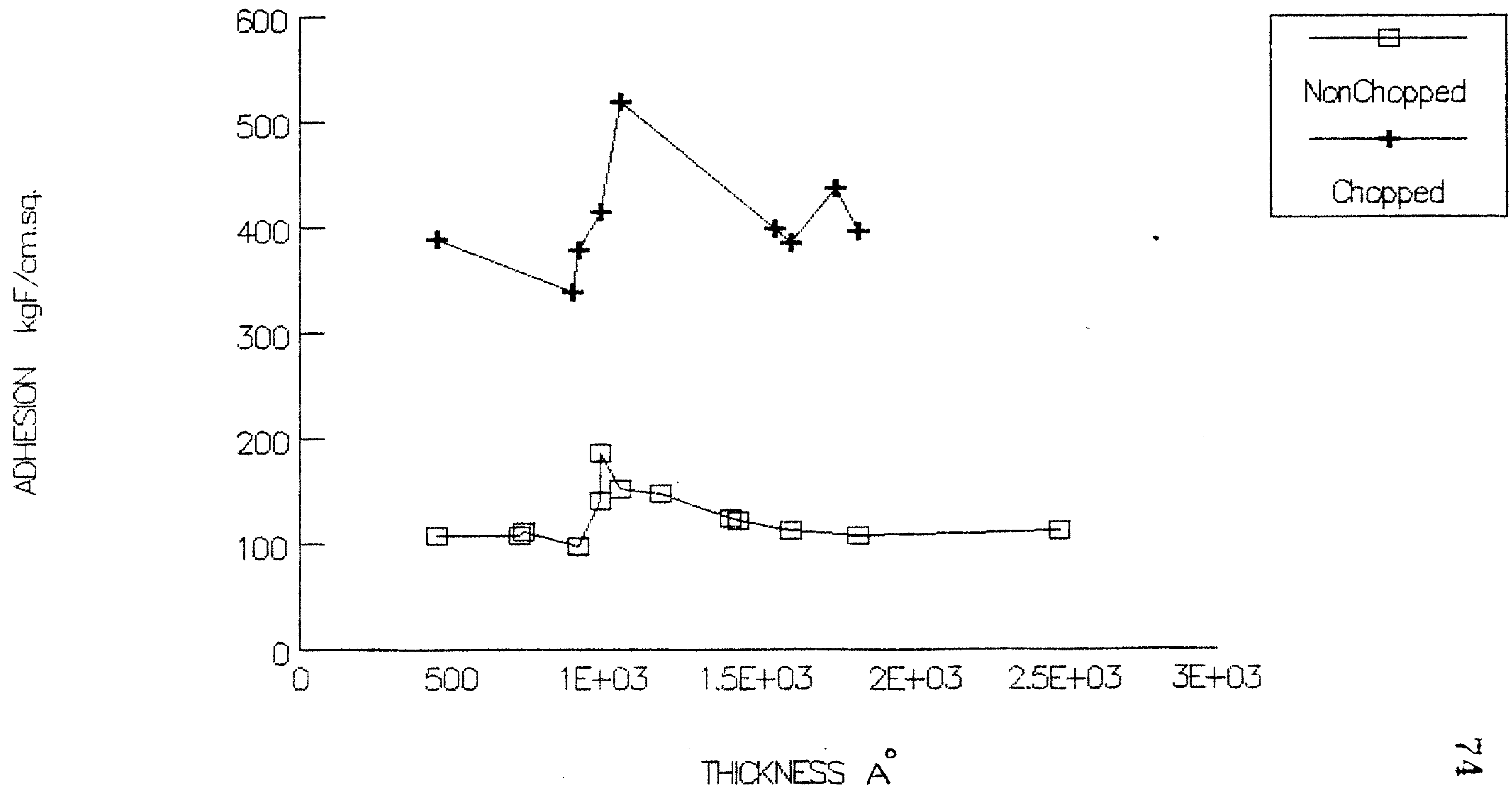

Fig. 3·3·2 (1)- AVERAGE VALUE OF ADHESION VS THICKNESS.

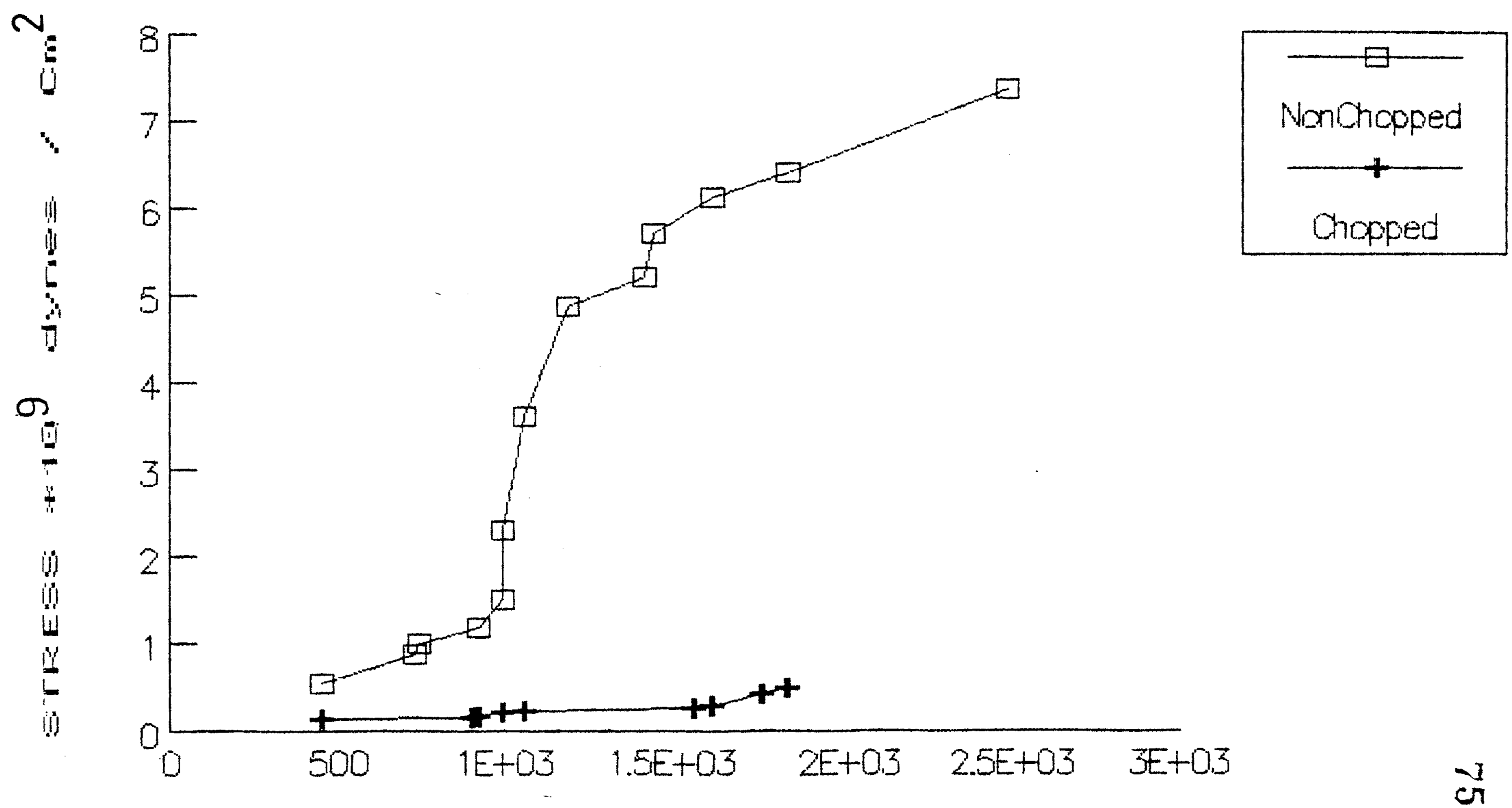

Fig. 3·3·2 (2) - AVERAGE VALUE OF STRESS VS THICKNESS .

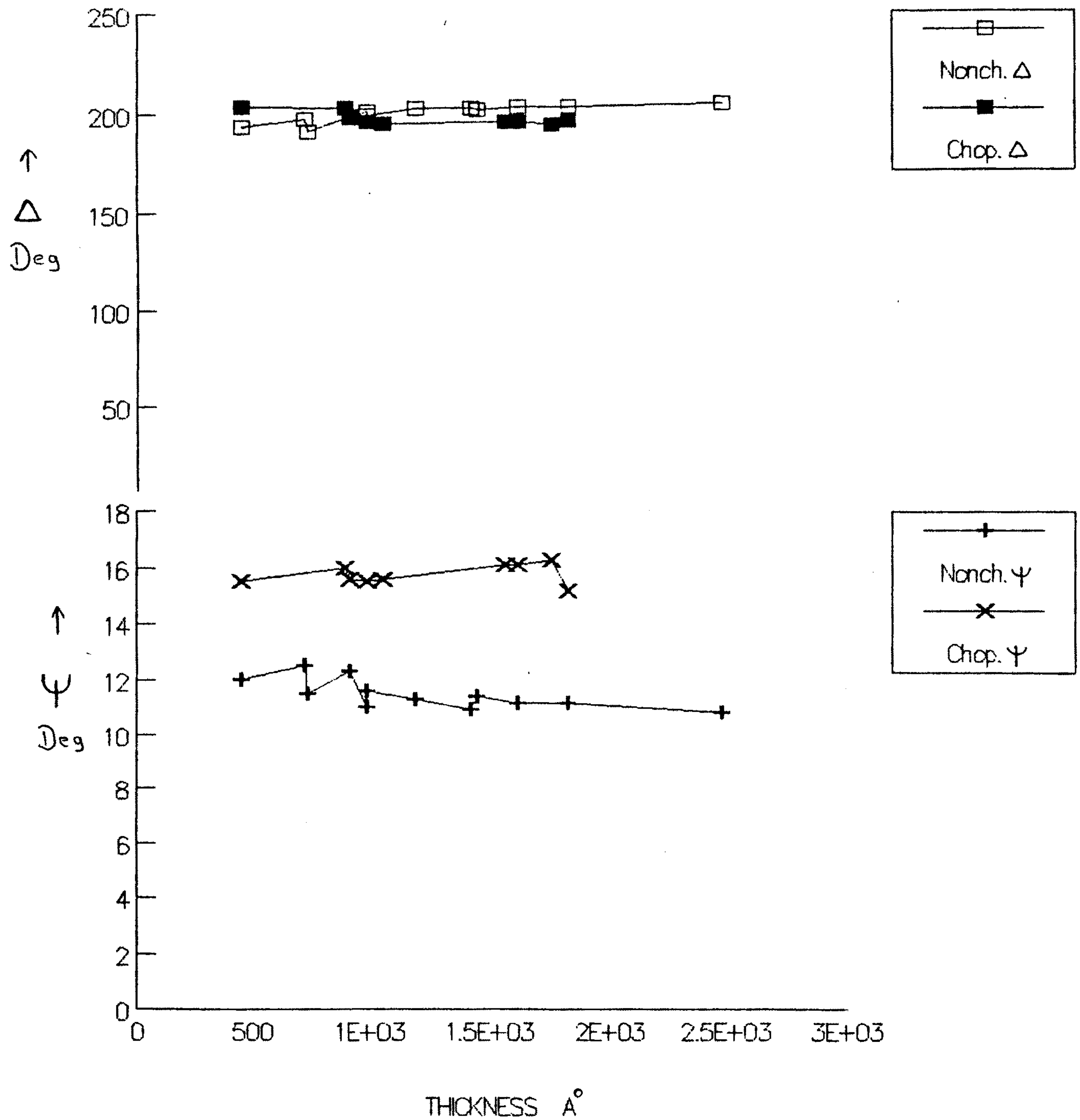

Fig- 3·3·2·(3) AVERAGE VALUES OF Δ, Ψ.

Where as for chopped films at one particular thickness ~ 1500 Å there is sharp increase in adhesion. Thicker films shows higher adhesion than thinner ones. As mentioned before chopped films in all the thickness ranges shows more than double adhesion as compared to nonchopped films.

The graph of stress Vs thickness that is fig.3.3.2 (2) shows remarkable changes in stress due to chopping. The value of stress for chopped films for all the thickness ranges lies between 0.13 to $0.50 * 10^9$ dynes / cm^2 with very little dependence on thickness, though thicker films shows slightly higher stress than thinner films. Where as for nonchopped films the stress rises rather steeply from 0.5 to $7.35 * 10^9$ dynes $/cm^2$ as thickness increases. It is seen that chopping helps in reducing the stress in films to very considerable amount.

Fig. 3.3.2(3) in which average data of (Δ),(Ψ) is plotted for various thickness ranges, shows similar results like fig - 3.3.1 (2).

3.3.3 AGING UNDER DIFFERENT AMBIENTS.

3.3.3.1 AGING IN AIR.

Only ellipsometric readings were taken for aging of cerium oxide films. The readings were taken repeatedly upto 180 days. The graph of typical values of (Δ),(Ψ) as function of time in days for chopped and nonchopped films are given in fig.3.3.3.1 (1).

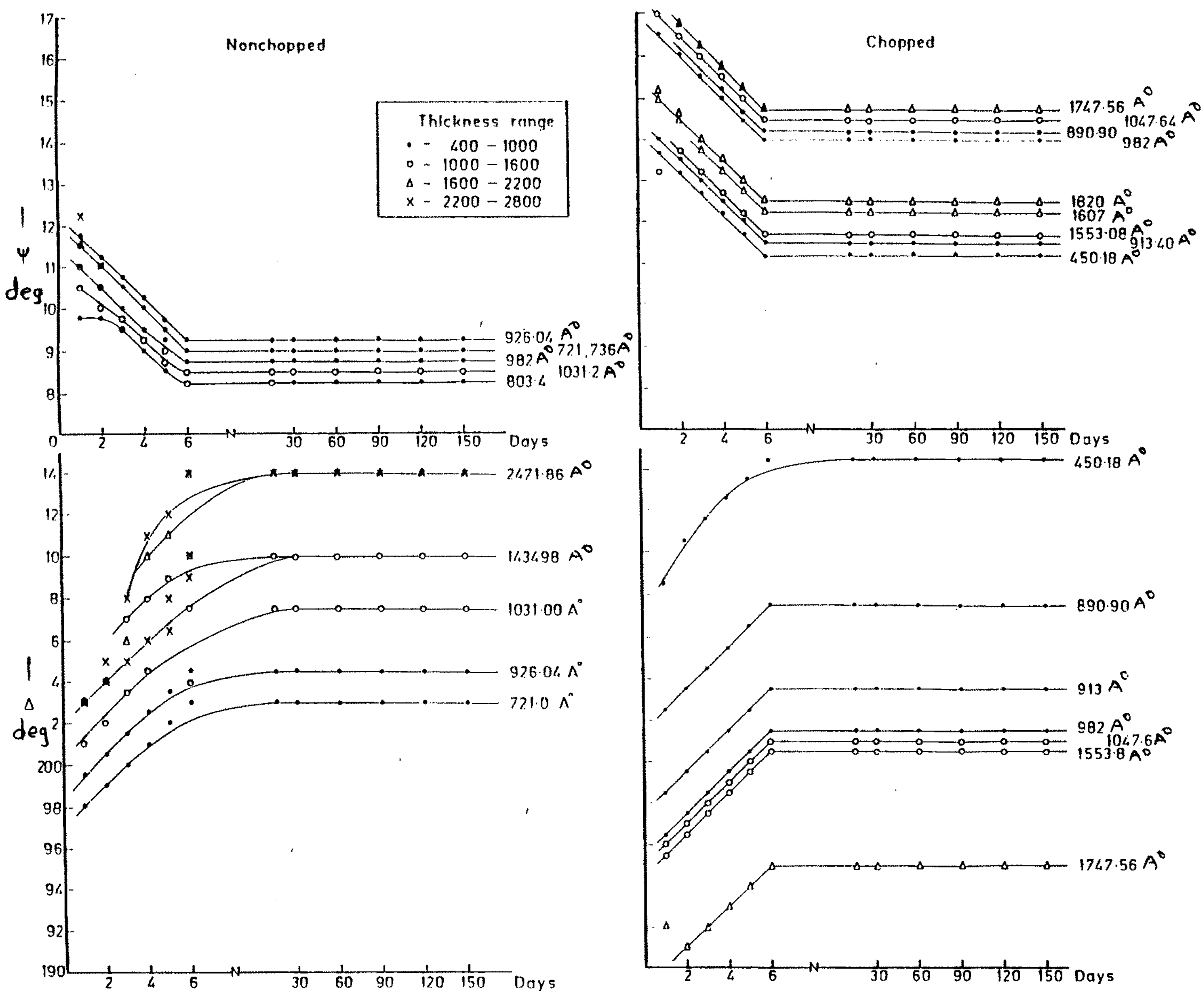

Fig. 3·3·3·1 (1) – Typical values of Δ, ψ as function of time in days for nonchopped and chopped films (Aging in air)

From the fig. it is seen that initially with in 6-days both for nonchopped and chopped films there is sharp increase in (Δ) and decrease in (Ψ), after there is almost no change. Changes in (Δ) for chopped films was slightly lesser than nonchopped films. For films of thickness 400-1600 Å both chopped and nonchopped films shows almost same change, where as for films above 1600 Å nonchopped films show higher changes (11) as compared to chopped films(5).

As far as changes in (Ψ) are concerned nonchopped and chopped cerium oxide films gives almost same values after aging in air. (Δ) of both fresh films and aged films show a definite thickness dependency. As thickness increases (Δ) increases for nonchopped films, where as reverse trend is shown in chopped films. (Ψ) shows random variation for both nonchopped and chopped films.

3.3.3.2 **EFFECT OF MOISTURE ON ADHESION AND (Δ), (Ψ).**

3.3.3.2 (a) **AGING IN ROOM TEMPERATURE MOISTURE.**

Though films were kept in room temperature moisture for three hours the adhesion measurements were taken only after 24 hours. Where as, for ellipsometric (Δ), (Ψ) values were taken immediately within five minutes after removal from ambient.

The values of adhesion Vs thickness before keeping in ambient and after keeping in ambient for nonchopped and chopped films are plotted in fig. 3.3.3.2(a)1

Fig. 3.3.3.2 (a) 2 gives the $\delta\Delta$, $\delta\Psi$ values as

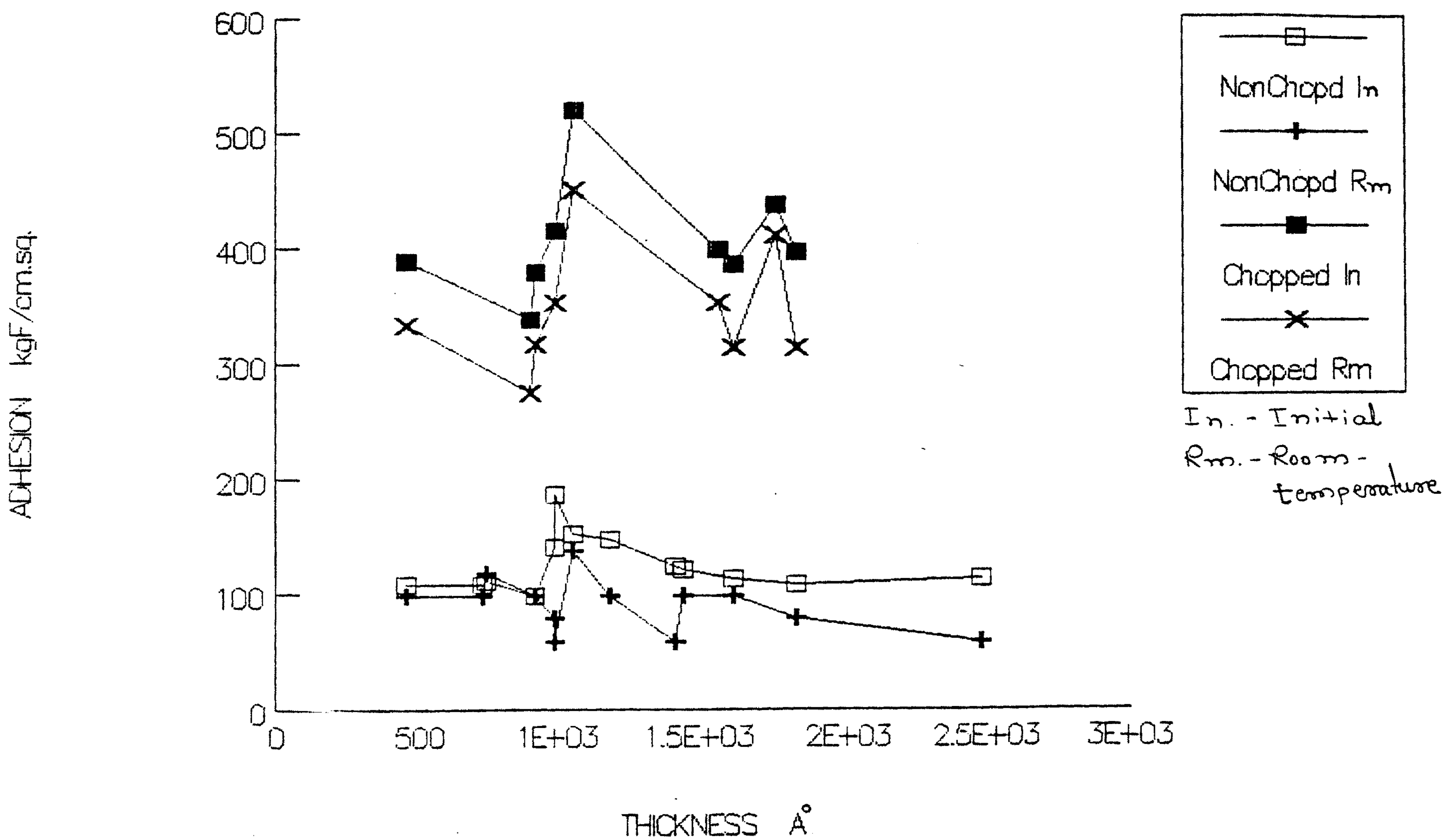

Fig. 3·3·3·2(a) 1 – ADHESION MEASUREMENTS.
EFFECT OF ROOM TEMP.

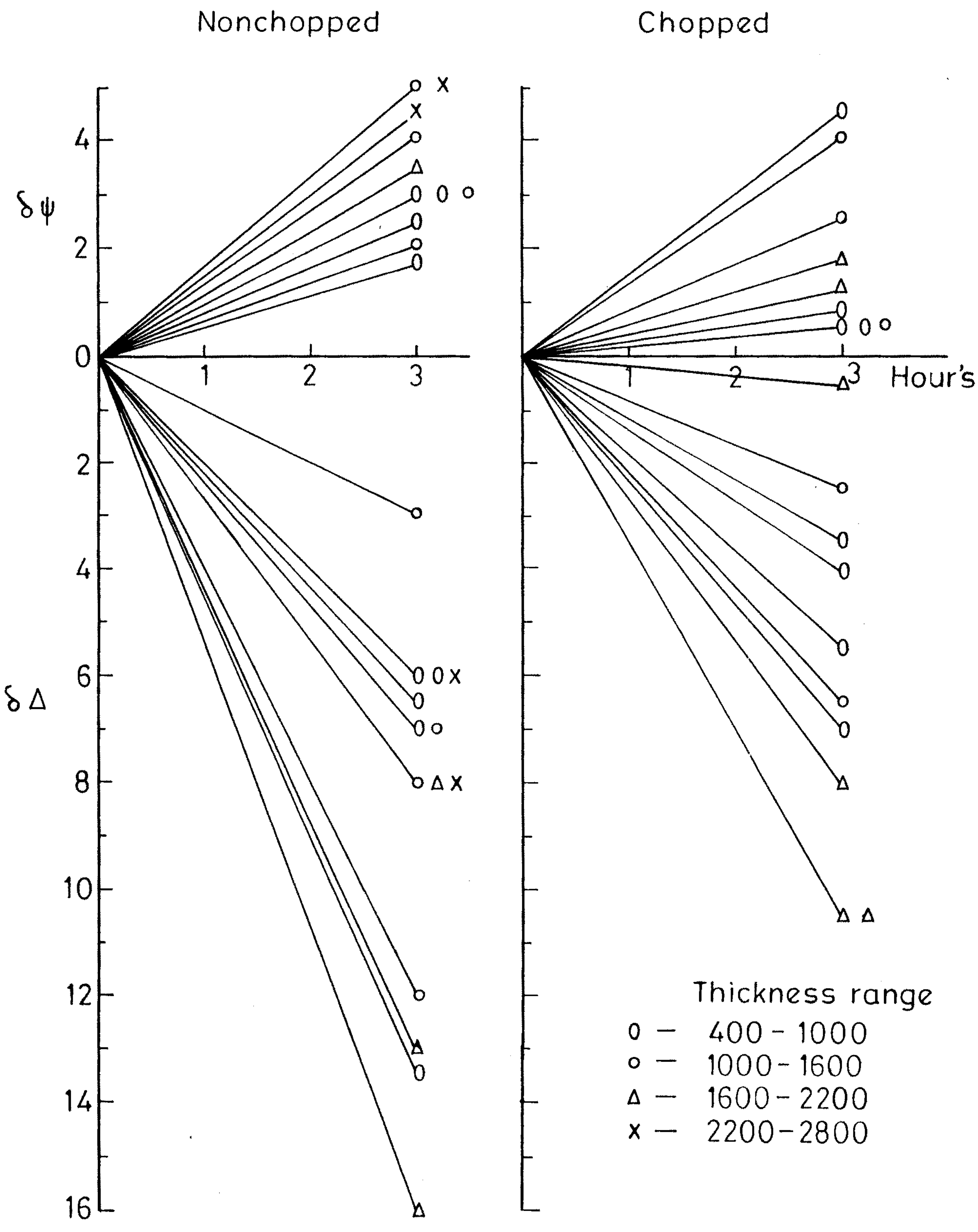

Fig. 3·3·3·2 (a) 2 – δΔ, δψ vs time in hour's for nonchopped and chopped films after effect of room temperature moisture.

a function of time. $\delta\Delta$, $\delta\Psi$ indicates the difference of (Δ) and (Ψ) respectively of fresh and aged films.

From fig. 3.3.3.2 (a) 1 it is seen that, for both nonchopped and chopped films adhesion decreases after room temperature moisture exposure. For films of thickness less than 1000 Å , nonchopped films shows very less change, almost with in the error limit of 9.8 KgF/cm^2 .

For the thickness range 1000-1600 Å there is sort of oscillatory behavior beyond which again there is smooth decrease, however the values of adhesion after room temperature moisture exposure are less than fresh films values.

However, for chopped films, the adhesion curve of both fresh and aged films follows similar pattern, except the value of adhesion becomes lower after aging.

From the ellipsometric data i.e. fig.3.3.3.2(a)2 it is seen that (Δ) decreases and (Ψ) increases for both nonchopped and chopped films. Changes in chopped films being lesser than that of nonchopped films.

Though all the ellipsometric readings were taken immediately after 3 hours of ambient exposure, some samples were kept for further aging of air for a long period of time around 180 days and then measurements of (Δ) and (Ψ) were taken after 180 days.

It is observed that, after 3 hours room

temperature exposure (Δ) was 184 and after 180 days (Δ) becomes 173 for nonchopped films and (Δ) for chopped films changes from 195 to 206 after 180 days.

(ψ) decreases from 14 to 7.5 for nonchopped films and for chopped films (ψ) changes from 19 to 13.

3.3.3.2 (b) **EFFECT OF COLD MOISTURE.(8 ^{o}c)**

Fig. 3.3.3.2 (b)1 shows the adhesion data and fig. 3.3.3.2 (b)2 shows ($\delta\Delta$) and ($\delta\psi$) data for aging of nonchopped and chopped cerium oxide films in cold moisture (8 ^{o}c).

Here as in room temperature moisture the adhesion decreases after ambient exposure. The changes being more in nonchopped films than that of chopped films for thickness ranges greater than 1000 $\AA$. For thickness less than 1000 $\AA$ the chopped films shows larger changes. Nonchopped films of lower thicknesses show an oscillator behavior.

The effect of cold moisture on adhesion is more than at room temperature moisture for nonchopped films. Thicknesses lesser than 1000 $\AA$ shows greater decrease in adhesion of chopped films than that of nonchopped films. For other thickness ranges the chopped films shows very less decrease almost with in experimental error at most of the thicknesses.

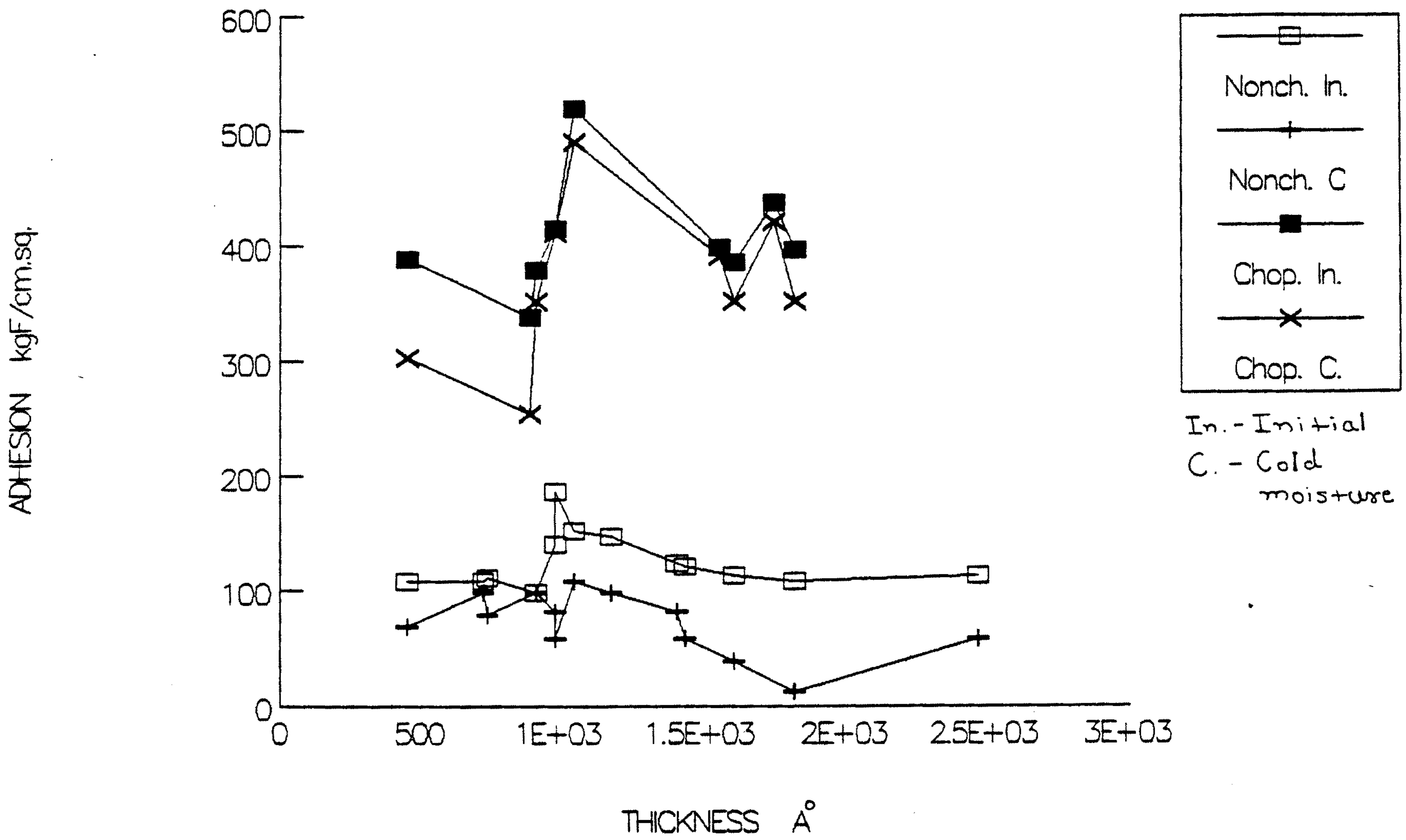

Fig. 3·3·3·2(b) 1 – ADHESION MEASUREMENTS.
EFFECT OF COLD MOISTURE

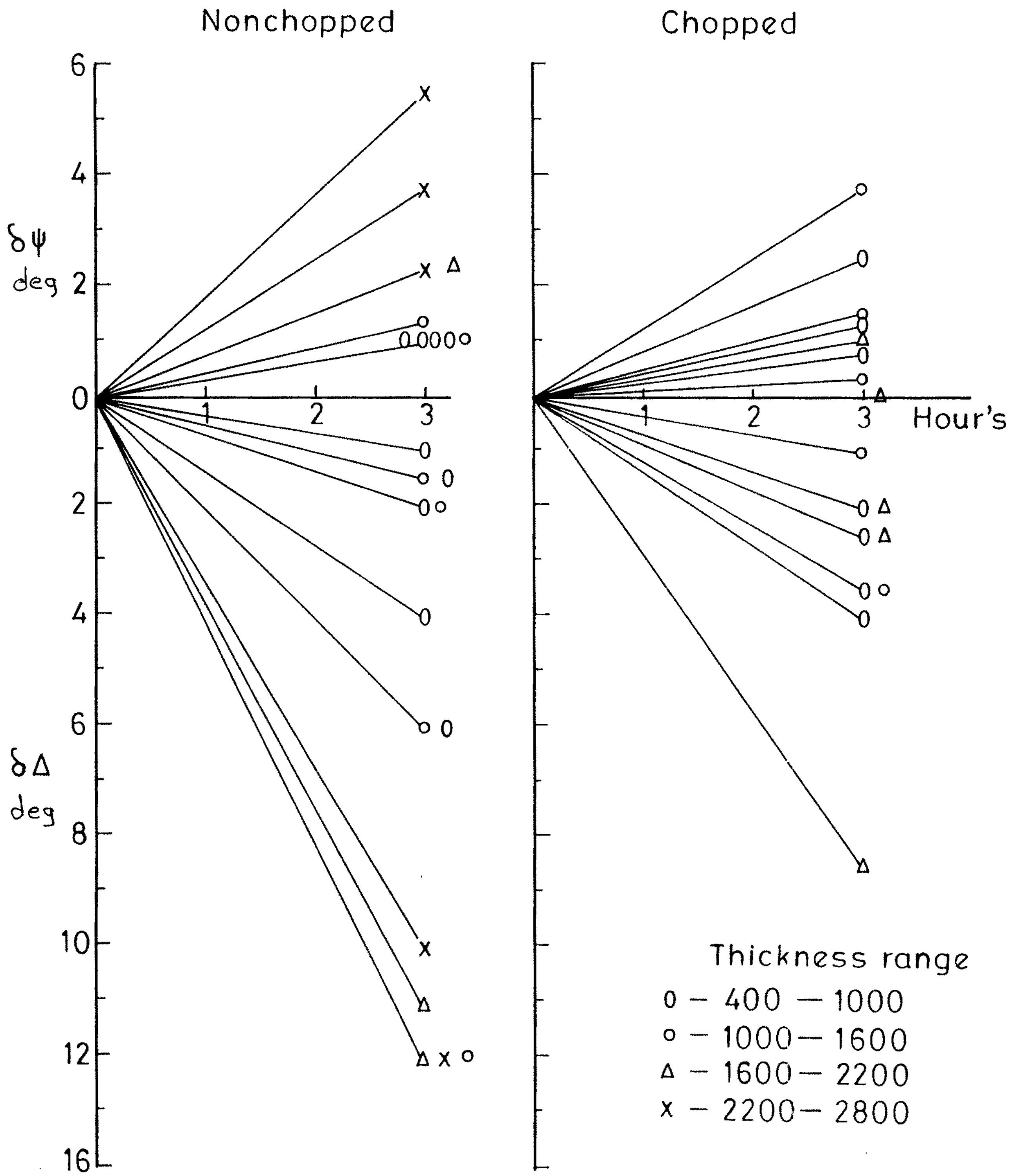

Fig. 3·3·3·2(b)2 – δΔ, δψ vs time in hours for nonchopped and chopped films after cold moisture effect.

From fig. 3.3.3.2(b)2 it is seen that, as expected (Δ) decreases and (Ψ) increases, similar to room temperature moisture. Here again chopped films shows lesser changes than that of nonchopped films. Films of thickness greater than 1600 Å show larger changes in (Δ) and (Ψ), for nonchopped films all the thickness show almost similar changes.

Though all the ellipsometric reading were taken immediately after 3 hours of ambient exposure some samples were kept for further aging of air for a long period of time around 180 days and then measurements of (Δ) and (Ψ) were taken after 180 days.

It is observed that, after 3 hours cold moisture exposure (Δ) was 188 and after 180 days (Δ) becomes 173 for nonchopped films and (Δ) for chopped films changes from 197 to 200 after 180 days.

(Ψ) decreases from 14 to 7.5 for nonchopped films and for chopped films (Ψ) changes from 18.5 to 13. after 180 days.

3.3.3.2 (c) <u>EFFECT OF SALTY MOISTURE AT ROOM TEMPERATURE.</u>

Fig.3.3.3.2(c)1 gives the graph of adhesion Vs thickness for aging in salty moisture.

Ellipsometric readings were not taken for this ambient. Here also just like other moisture ambients the adhesion decreases for both chopped and nonchopped films.

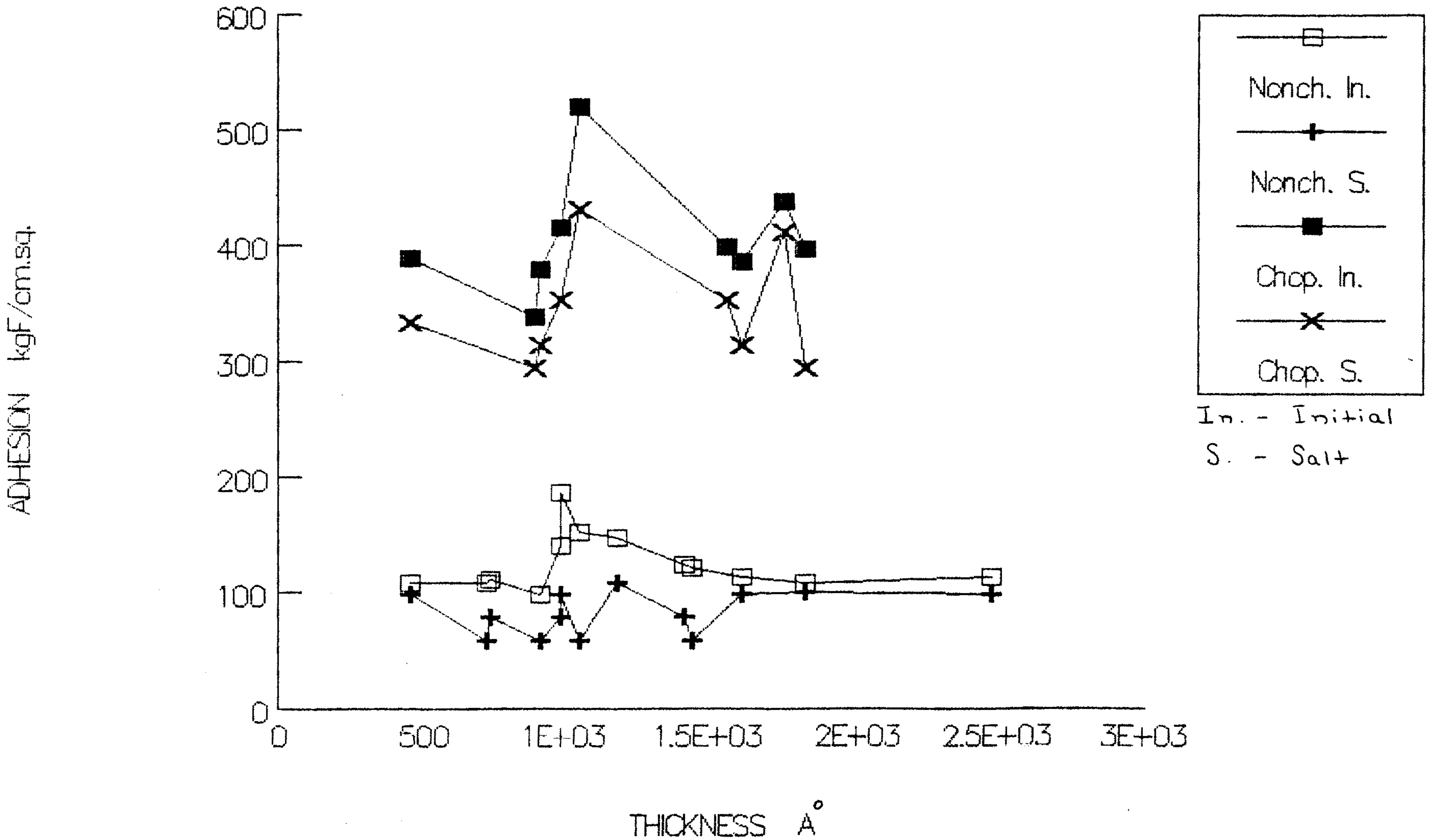

Fig. 3·3·3·2 (c)1– ADHESION MEASUREMENTS.
EFFECT OF SALTY MOISTURE

The adhesion shows a oscillatory behaviour for thicknesses less than 1800 Å for nonchopped films, where as no such oscillatory behaviour is shown in chopped films.

The decrease in adhesion for thickness higher than 1800 Å is very less for nonchopped films where as it is more for chopped films.

3.3.3.3 **EFFECT OF HEAT. (120 °c)**

Fig 3.3.3.3(1) shows the plot of adhesion for various thickness ranges for aging in heat. Here reverse phenomenon is observed as that of moisture. After ambient effect adhesion increases in both nonchopped and chopped films.

The curve of aged films of chopped cerium oxide is same as that of fresh films, where as in nonchopped films it shows some oscillatory behaviour for thinner films.

From fig. 3.3.3.3.(2) it is observed that also in measurement of (Δ) and (Ψ) it shows reverse effect as that of moisture, after exposure to heat. In this case (Δ) increases while (Ψ) decreases.

Though all the ellipsometric readings were taken immediately after 3 hours of ambient exposure, some samples were kept for further aging of air for a long period of time around 180 days and then measurements of (Δ) and (Ψ) were taken after 180 days.

It is observed that, after 3 hours exposure to

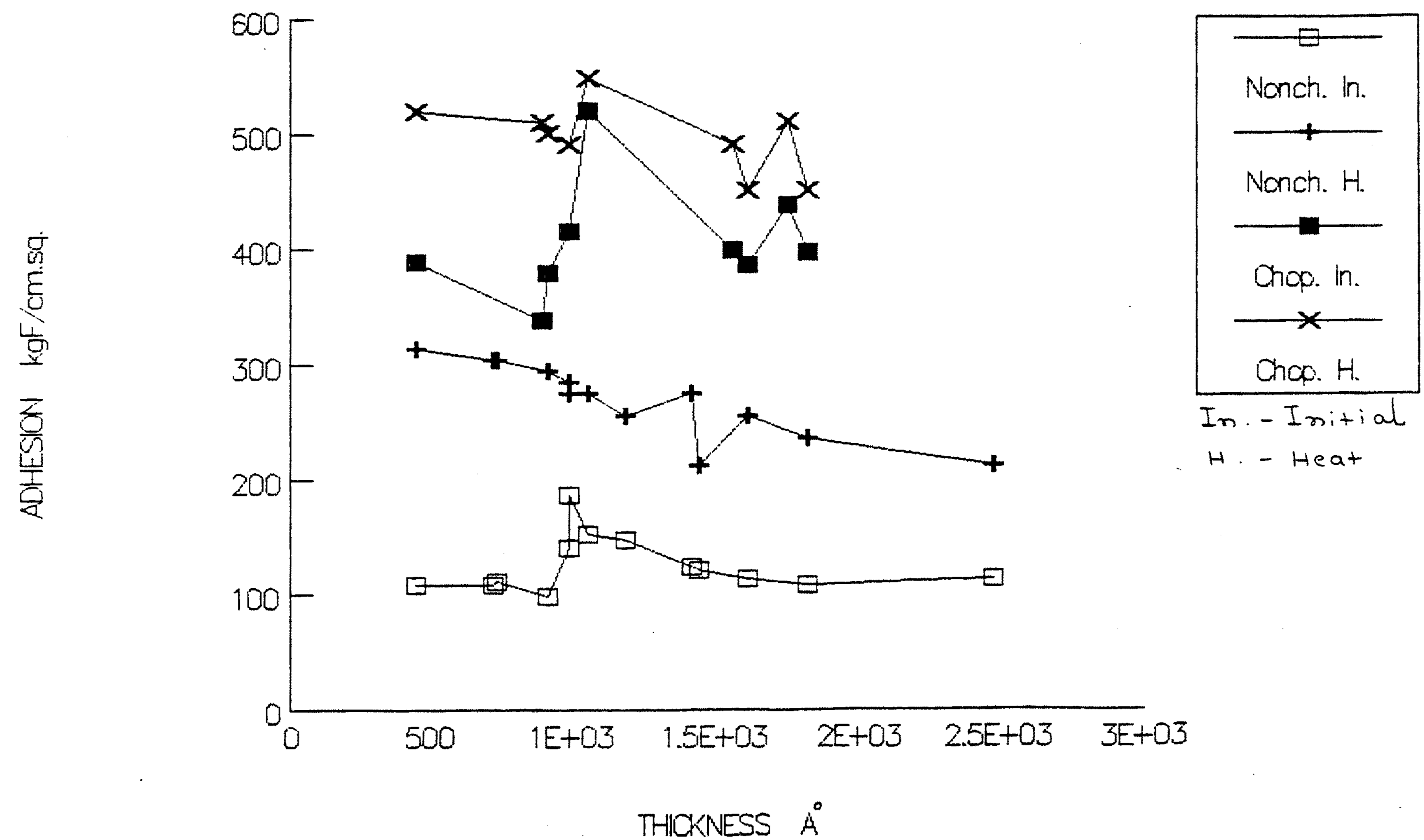

Fig. 3·3·3·3 (1) - ADHESION MEASUREMENTS. EFFECT OF HEAT

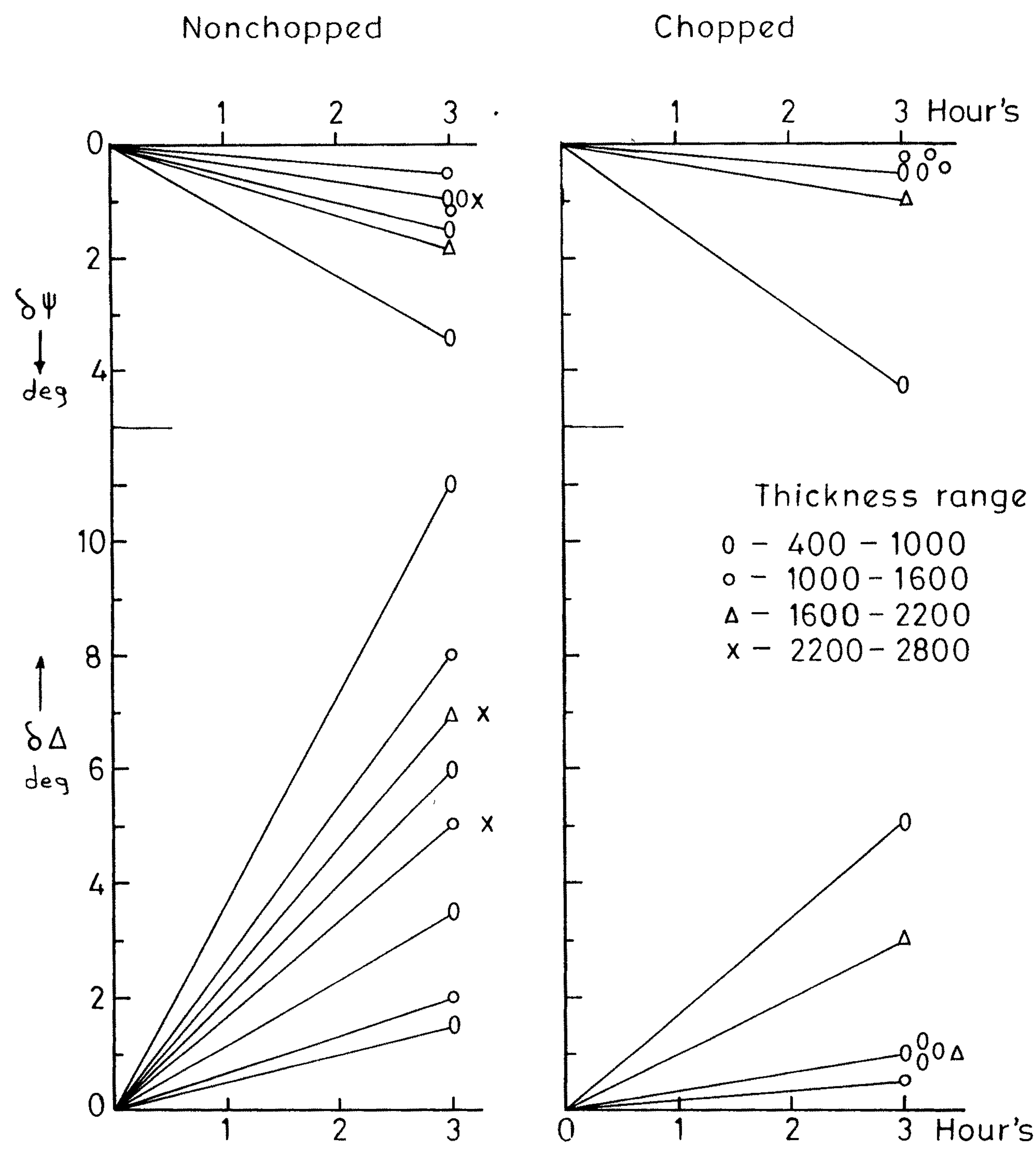

Fig. 3·3·3·3(2) – δΔ, δψ vs time in hours for nonchopped and chopped films after effect of heat.

heat (Δ) was 196 and after 180 days (Δ) becomes 176 for nonchopped films and (Δ) for chopped films becomes 199 to 190.

For nonchopped films (Ψ) changes form 11 to 18 and for chopped films (Ψ) changes from 17.5 to 18.

3.3.3.5 **SUMMARY OF SOME IMPORTANT RESULTS.**

The summary of the results observed, from the investigations carried out are as follows.

The average values of the various data grouped under different thickness ranges have been given in Table 3.3.3.4.

Some of the important observations are,

1) Adhesion of chopped cerium oxide films is more than twice higher than that of nonchopped film irrespective of thickness of the film.
2) Stress of chopped films is considerably decreased as compared to nonchopped films.
3) The thickness dependency of stress of nonchopped films is almost absent in chopped films.
4) The value of (Δ) increases with thickness for nonchopped films and (Δ) decreases for chopped films. Nonchopped cerium oxide film have lower (Ψ) values as compared to chopped cerium oxide films.
5) Initially (till 6 days) aging in air is very fast,

steep increase in (Δ) and decrease in (Ψ) afterwards there is no change.

6) All the three moisture, ambients decrease the adhesion and (Δ), where as (Ψ) increases. Adhesion shows thickness dependent changes.

7) A Very interesting result obtained is that in the thickness range 1000 - 1600 Å for all the ambients studied chopped films show lesser adhesion changes than nonchopped films which is not the case for other thickness ranges.

8) After 3 hr's exposure to heat chopped films shows lesser adhesion changes than that of non chopped films in every thickness range.

9) Heating the film in air increases adhesion and (Δ), where (Ψ) decreases.

10) In all the ambients the changes in (Δ)and(Ψ) are less for chopped films.

Table: 3.3.3.4
Average values of available data

Ambient	Time	Property	400-100Å		1000-1600Å		1600-2200Å		2200-2800Å	
			Non-chopped	Chopped	Non-chopped	Chopped	Non-chopped	Chopped	Non-chopped	Chopped
Fresh film		Adhesion KgF/cm^2	130.99	380.15	170.52	458.96	112.7	406.74	110.25	-
		Stress $10^{11} dynes/cm^2$	1.02	0.16	4.33	0.25	6.10	0.39	6.87	-
		Δ	196.18	199.84	201.03	194.94	202.68	194.73	203.3	-
		ψ	11.86	15.65	11.3	15.84	11.16	15.83	10.98	-
Air	After \`2' day's	$\delta\Delta$	2.4	2.5	1.25	2	1	3	1.5	
		$\delta\psi$	0.9	1.18	0.62	1	0.5	1	0.75	
	After \`6' day's	$\delta\Delta$	7	6.5	6.25	6	4	7	6	
		$\delta\psi$	3.25	3.06	2.18	2.12	3.5	2.33	3.5	
	After \`30' day's	$\delta\Delta$	7	6.5	6.25	6	4	7	6	
		$\delta\psi$	3.25	3.06	2.18	2.12	3.5	2.33	3.5	

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Ambient	Time	Property	Thickness ranges 400-100A°		1000-1600A°		1600-2200A°		2200-2800A°
	After `120' day's	$\delta\Delta$	7	6.5	6.25	6	4	7	6
		$\delta\psi$	3.25	3.06	2.18	2.12	3.5	2.33	3.5
Room temp. Moisture		Adhesion	98	318.5	88.2	401.8	98	346.2	78.4
		$\delta\Delta$	8.1	4.75	6.25	4.5	16	9.3	15
	After `3' hour's	$\delta\psi$	2.7	1.75	3.125	2.25	4.75	3.75	5
	After '6' months	$\delta\Delta$	14	3	37	4	33	5.5	
		$\delta\psi$	4	5.25	4	1.5	4.75	3	
Cold moisture		Adhesion	86.24	330.75	88.2	441	58.8	378.93	36.75
	After `3' hour's	$\delta\Delta$	2.9	3	2.8	2.75	11	4.3	11
		$\delta\psi$	1	1.3	0.9	2.1	2.25	3	4.125
	After `6' months	$\delta\Delta$	27	5	36	2	29	3.5	
		$\delta\psi$	5	2.5	4.5	0.75	5.75	2.75	

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			Thickness ranges						
Ambient	Time	Property	400-100Å		1000-1600Å		1600-2200Å		2200-2800Å
Salty moisture		Adhesion	74.48	323.4	284.2	392	58.8	339.73	98.66
Heat		Adhesion	299.88	504.7	269.5	519	211.68	470.4	233.89
	After `3' hour's	$\delta\Delta$	5.2	1.5	3.75	1	1	1.5	5.5
		$\delta\psi$	1.5	1.4	0.875	0.5	1.75	0.5	1
	After `6' months	$\delta\Delta$	2.5	8	25	21	24	21	
		$\delta\psi$	6.25	0.25	7.25	1	7.25	0.75	