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ZIRCONIUM ALLOYS IN TERPHENYLS

by

G. IMARISIO

1965

Joint Nuclear Research Center
Ispra Establishment - Italy

Physical Chemistry Service

Paper presented at the ANS winter meeting 1964
San Francisco, California

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A statistical planning and analysis has been chosen because of the high number of variables.

The corrosion experiments have been done in a group of eight thermosiphon loops with terphenyl at 380° C. and 420° C.

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2) Time
3) Chlorinated impureties concentration.

Enough dissolved water must be present to assure a normal oxidation of the Zirconium alloy. Zr. 3 Nb - 1 Sn has shown an anormalous corrosion behaviour in terphenyl.

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ZIRCONIUM IN TERPHENYLS (°)

1) Introduction

The possible use of Zirconium alloys as a material for pressure tubes and canning in the Orgel reactor instead of SAP was considered at the beginning of 1963.

At that time the data on corrosion behaviour of these alloys in terphenyls were negative (1,2,3,4), but also somewhat scattered and contradictory.

Recent data (5,6) show better promises and in view of the very great interest of these alloys for the Orgel project it was decided to perform a series of systematic screening measurements on the corrosion behaviour of a few Zirconium alloys in terphenyls.

As a working hypothesis it was assumed that the water dissolved in the organic at working temperature (around 400° C) should behave almost like steam at the same partial pressure and temperature.

On this basis the choice of alloys was restricted to those developed for water or steam service.

For this part of the research, Zircaloy-2 and Zr-3 Nb-1 Sn* were chosen, the first because its properties are well known and

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* Zircaloy-2: 1,5 % Sn; 0,12 % Fe; 0,05 % Ni; 0,10 % Cr, balance Zr.

Zr-3 Nb-1 Sn, an alloy developed under Euratom contract by Metallgesellschaft A.G., Frankfurt / Germany.

(°) Manuscript received on August 12, 1965

because it is very often used as a comparison term to the other alloys; the second as a choice among new alloys under development because it was immediately available.

The main purpose of this research was to investigate the significance of the many parameters involved in corrosion of zirconium alloys in terphenyls (and of their eventual interactions).

Previous experience has shown that the corrosion in organics depends on:

1) Temperature
2) Time of exposure
3) Water concentration
4) Chlorine "
5) Hydrogen partial pressure
6) Surface conditions.

It was obvious that a "classical" planning would have required a very long time for the screening. So it was decided to perform a statistical planning and analysis in order to obtain the maximum amount of information from the measurements.

2) Planning of the experiments

A factorial plan was chosen and the fifth factor (the hydrogen partial pressure) was omitted after some preliminary results showed that it was not important, at least if enough dissolved water is present in the organic.

To reduce further the number of experiments, samples with the two surface treatments chosen, were included in all the experiments.

This leads to 16 experimental units for a 2^5 factorial plan.

For further reducing of the time needed to complete the screening, eight experimental facilities had to be provided. Table 1 shows the complete statistical design.

The first column shows the standard symbolic representation of each experimental unit, expanded in the following columns into an operative table in which the signs + and - indicate respectively the higher and lower levels assumed by the factor shown on top of the column.

The actual values of the six factors are reported in Table 2.

3) Corrosion loops

The corrosion measurements were performed in eight stainless steel thermosiphon loops, divided into two plants grouping four loops each.

The two plants have independent feeding facilities and electrical controls; the plants are electrically trace-heated. Fig. 1 shows a sketch of one loop.

The main expansion tank R contains 2/3 of the total holdup of the loop.

A gas stream (N_2) saturated with water in the saturator Ws bubbles through the terphenyl of the tank.

This makes the concentration of water, dissolved in the terphenyl, fairly well constant.

The water temperature in the saturator determines the water concentration of terphenyl.

An electric heater H brings the fluid to working temperature.

A finned tube cooler, C, lowers this temperature of about 10-20° C to obtain a thermosiphon circulation.

The velocity of the fluid in the test section at this temperature difference is around 10-15 cm/sec.

Two test sections, T_1 and T_2, are provided; terphenyl drain D, sampling S and feeding F complete the loop.

The nitrogen is discharged through the vent V after the terphenyl vapours are condensed in Cd.

All the electrical switching and control apparatus are centralized in the control desks.

Automatic continuous operation is provided without surveillance.

Fig. 2 shows a close view of one of the loops, Fig. 3 a general view of a group of four loops. Fig. 4 shows the control room and desks. Maximum operating conditions of the loops are:

- temperature 420° C;
- pressure 15 kg/cm^2;
- flow-rate 15 cm/sec.

4) Sample preparation

The sample source material has always been in sheet form.

Marking and identification were done on the sheets before cutting.

A blank sample was always left between two successive corrosion samples to control the initial hydrogen content of the metal.

The blanks were treated like the corresponding corrosion samples but for the exposure to the terphenyl.

Enough samples were marked for the complete series of experiments.

A random choice between all the samples was carried out to assign the group of samples to every experimental unit.

Each group of samples and blanks was given a standard pickle and heat treatment.*

The preoxidized samples were oxidized in dry oxygen at the same temperature as the subsequent corrosion experiment. The weight gains for the preoxidation were 7 - 8 $\frac{mg}{dm^2}$ for Zr-2 and 11 - 12 $\frac{mg}{dm^2}$ for Zr-3 Nb-1 Sn.

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* Pickle: Zr-2 HF(35%); 5,2 p by volume; HNO_3(65%) 49 p.b.v. H20 45.8 p.b.v.

Zr-3 Nb-1 Sn HF(37%) 14 p.b.v.; HNO_3(65%) 76 p.b.v. H_2O 10 p.b.v.

Stop: $Al(NO_3)_3 \cdot 9\ H_2O$; 150 g; HNO_3(65%), 7 cc, H_2O to 1000 cc.

Heat treatment: Zr-2 750° for one hour at 10^{-6} torr; Zr-3 Nb-1 Sn 590°C for 2 hours at 10^{-6} torr.

After weighing the samples were mounted on a special sample holder, shown in Fig. 5. A string of 9 sample holders was then inserted in each test section.

After the experiment, the samples were cleaned from terphenyl by means of xylene refluxing in Kumagawa extractors before weighing and H analyses.

5) Results

The weight gains of the samples were not always obtainable because severe oxyde spalling was observed at the higher temperature and chlorine concentrations.

As a consequence, the first analysis of the results has been done on the hydrogen weight gains only. Table 3 summarizes the statistical analysis of the whole experiment.

The first column shows the standard symbolic representation of the 16 measurements. The effect means are reported in the following columns for each treatment for the two alloys. A single asterisk indicates the effects significant at the 5 % level. A double asterisk indicates the effects significant at the 1 % level.

The significant factors for the Zr-2 corrosion in organic are: 1) temperature; 2) time of exposure; 3) chlorine concentration; and some of the related multiple factor interactions up to the four-factor one.

The other factors and interactions are not significant. The significant factors for Zr-3 Nb-1 Sn are: 1) water concentration; 2) time of exposure; 3) temperature; 4) chlorine concentration; and

all the related multiple factor interactions, up to the four-factor one.

An increase of water concentration lowers the hydrogen pick-up; this fact seems to suggest that the water concentration was not high enough to allow a normal oxidation to take place for this alloy.

In fact, an oxide not well compact could have produced the higher corrosion observed because of an inefficient protection.

This alloy shows also interactions with negative sign between the water and the other factors. This fact seems to confirm the insufficiency of the water concentration.

The working hypothesis of a similarity between the corrosion of the alloys or zirconium in steam and in terphenyl has not been confirmed.

In fact the results reported in Table 3 show big differences between the two alloys examined, the ZrNbSn alloy being the worse, while in steam it is the best one.

Separate experiments in autoclaves and in small steam loops at low pressure have confirmed the situation pointed out here.

It seems probable that to obtain good results in terphenyl for this alloy, a higher water concentration will have to be present.

The metallographic examination of the samples further confirms the above reported comments.

The results of the metallographic examination are shown in Fig. 6 for Zr-3Nb-1Sn (polarized light X 1100) and Fig. 7 for

Zircaloy-2 (polarized light X 1100). Fig. 8 shows the oxide on Zr-2 corroded at 380°C as pickled at for 15 days in low chlorine terphenyl. The oxide, compact and fairly uniform, is ~1 μ thick.

The same metal is shown in Fig. 9 after corrosion as pickled at 420°C for 30 days with low chlorine concentration. Oxide average thickness is ~1,6 μ. The oxide is compact but of not-uniform thickness. Fig. 10 shows a different sample of Zr-2 corroded in the same conditions, the thickness is ~ 2,3 μ and the oxide shows some cracks. Fig. 11 shows a Zr-3Nb-1Sn sample after corrosion as pickled at 400° C for 30 days in low chlorine terphenyl. The oxide was badly spalled.

The same metal in the same conditions but for 15 days of exposure, is shown in Fig. 12. The oxide is ~4,7 μ thick, very irregular and cracked.

Fig. 13 shows the same metal corroded as pickled for 15 days at 360°C with a low chlorine concentration.

The oxide layer is very poor, ~1,8 μ thick.

It is evident that the oxide grown on Zr-Nb-Sn has a much poorer appearance than the one developed on Zr-2, in spite of the less severe corrosion conditions (400°C instead of 420°C, 360°C instead of 380°C).

6) Conclusions and future work

This research has shown that some differences are to be expected between the corrosion behaviour of Zr-alloys in steam and the corrosion in terphenyl containing water.

It has been shown that a limited number of parameters is significant for the corrosion of Zr-alloys in terphenyls, namely: 1) temperature; 2) time of exposure; 3) water concentration; 4) chlorine concentration.

It seems that the water content of terphenyl needs to be higher than a minimum value, under which the corrosion is not regular. Once this minimum level has been reached, no further effects seem to be present.

The short term tests used for this research do not give enough information on the alloys investigated for a long time in reactor use, because the long term corrosion will be mostly in the post-transition region, here not well investigated.

A complete long-term experiment is under preparation for the next year at the Euratom research establishment at Ispra, Italy.

A series of Zr-alloys, developed for high temperature steam service will be corrosion-tested in high-temperature terphenyl with the above significant parameters as variables.

Collateral runs in superheated steam at atmospheric pressure will be done for the comparison of the two types of corrosion behaviour.

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Table 1

EXP.			Levels of the factors shown				
			A	C	D	E	F
1	(1)	or f	-	-	-	-	$\frac{-}{+}$
2	a	" af	+	-	-	-	$\frac{-}{+}$
3	c	" cf	-	+	-	-	$\frac{-}{+}$
4	ac	" acf	+	+	-	-	$\frac{-}{+}$
5	d	" df	-	-	+	-	$\frac{-}{+}$
6	ad	" adf	+	-	+	-	$\frac{-}{+}$
7	cd	" cdf	-	+	+	-	$\frac{-}{+}$
8	acd	" acdf	+	+	+	-	$\frac{-}{+}$
9	e	" ef	-	-	-	+	$\frac{-}{+}$
10	ae	" aef	+	-	-	+	$\frac{-}{+}$
11	ce	" cef	-	+	-	+	$\frac{-}{+}$
12	ace	" acef	+	+	-	+	$\frac{-}{+}$
13	de	" def	-	-	+	+	$\frac{-}{+}$
14	ade	" adef	+	-	+	+	$\frac{-}{+}$
15	cde	" cdef	-	+	+	+	$\frac{-}{+}$
16	acde	" acdef	+	+	+	+	$\frac{-}{+}$

A = water concentration
C = Temperature
D = Time of exposure
E = Chlorine concentration
F = Surface conditions
+ = higher level
- = lower level

Table 2

ACTUAL VALUE OF FACTORS

Factor		Lower level	Upper level
A	Water concentration	20 - 30 ppm	60 - 80 ppm
C	Temperature	380°C (Zr-2) 360°C (Zr, Nb, Sn)	420°C (Zr-2) 400°C (Zr, Nb, Sn)
D	Time	15 days	30 days
E	Chlorine concentration	0,2 - 0,4 ppm	1,5 - 2 ppm
F	Surface conditions	pickled	preoxidized

Table 3

Treatment	Effect means Δ H/S, mg/dm^2			
	Zircaloy-2		Zr3Nb1Sn	
(1)	115		98	
a	-1		-52	**
c	220	**	193	**
ac	7		-51	**
d	70	**	37	**
ad	70	**	32	**
cd	62	**	36	**
acd	78	**	34	**
e	228	**	189	**
ae	-1		-48	**
ce	219	**	186	**
ace	7		-47	**
de	70	**	34	**
ade	70	**	34	**
cde	62	**	33	**
acde	78	**	36	**
f	-10		0	
af	13		5	*
cf	-7		0	
acf	10		5	*
df	9		2	
adf	-6		0	
cdf	12		2	
acdf	-10		0	
ef	-10		0	
aef	13		4	*
cef	-7		1	
acef	10		4	*
def	9		2	
adef	-6		1	
cdef	12		2	
acdef	-10		1	

A single asterisk indicates the effects significant at the 5% level;
a double asterisk indicates the effects significant at the 1% level.

A = Water concentration
C = Temperature
D = Time of exposure
E = Chlorine concentration
F = Surface conditions

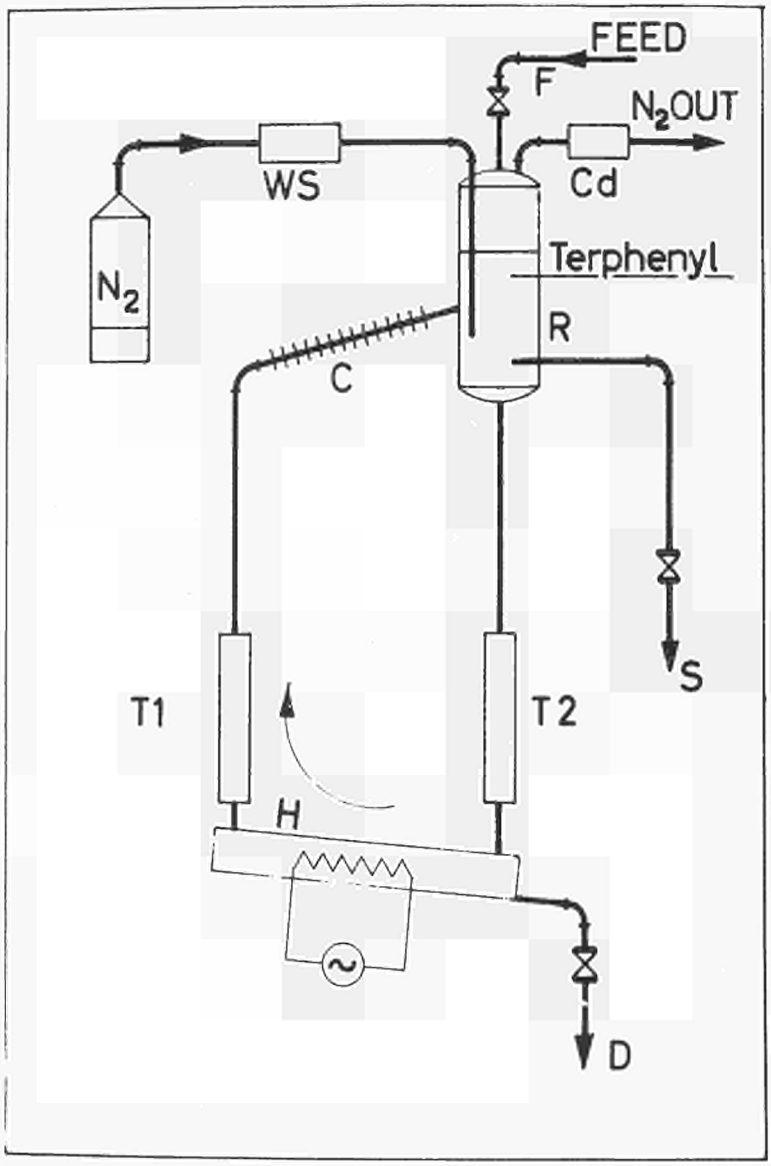


Fig. 1 : Sketch of one thermosiphon loop

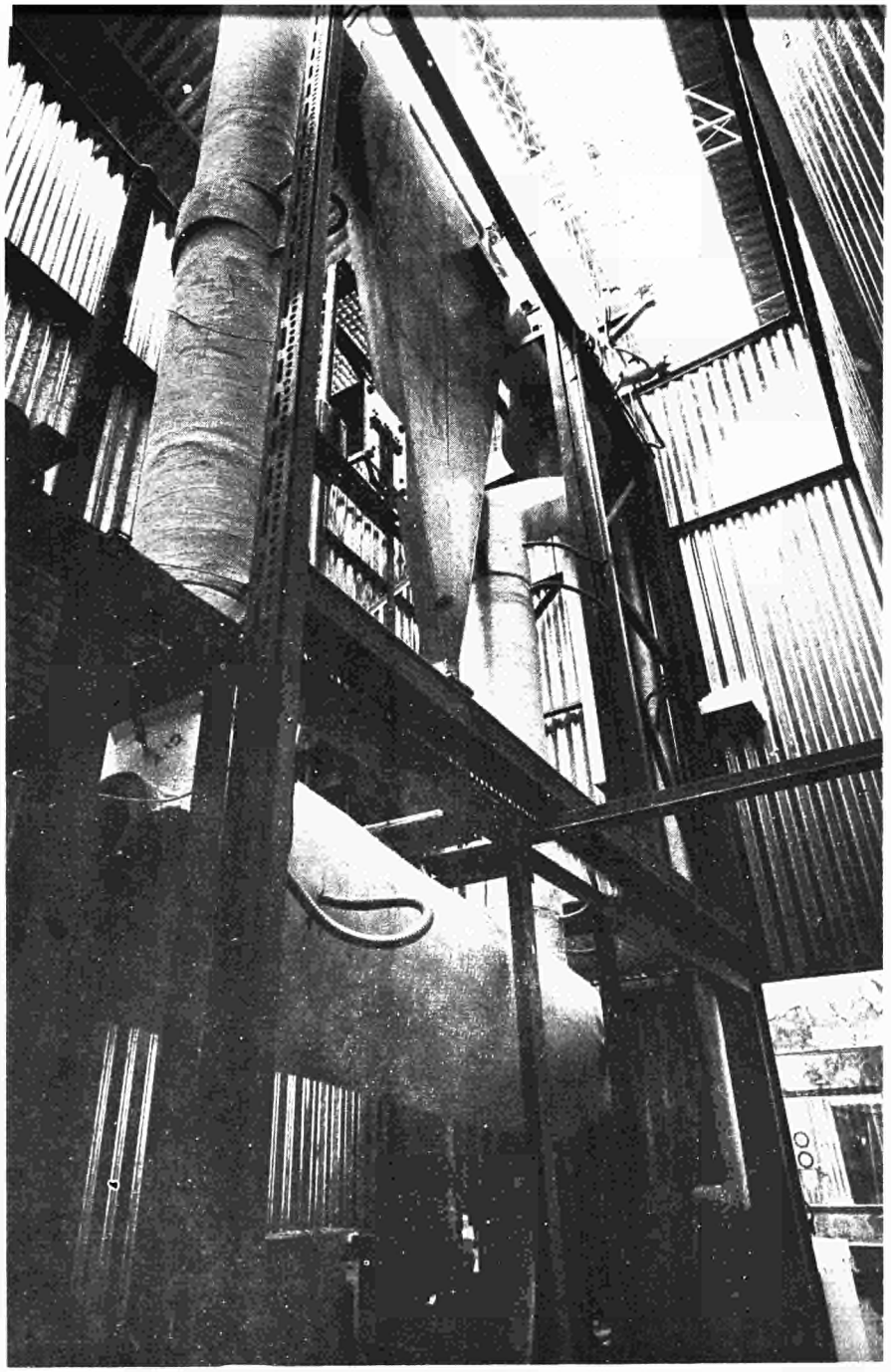


Fig. 2 : View of one loop

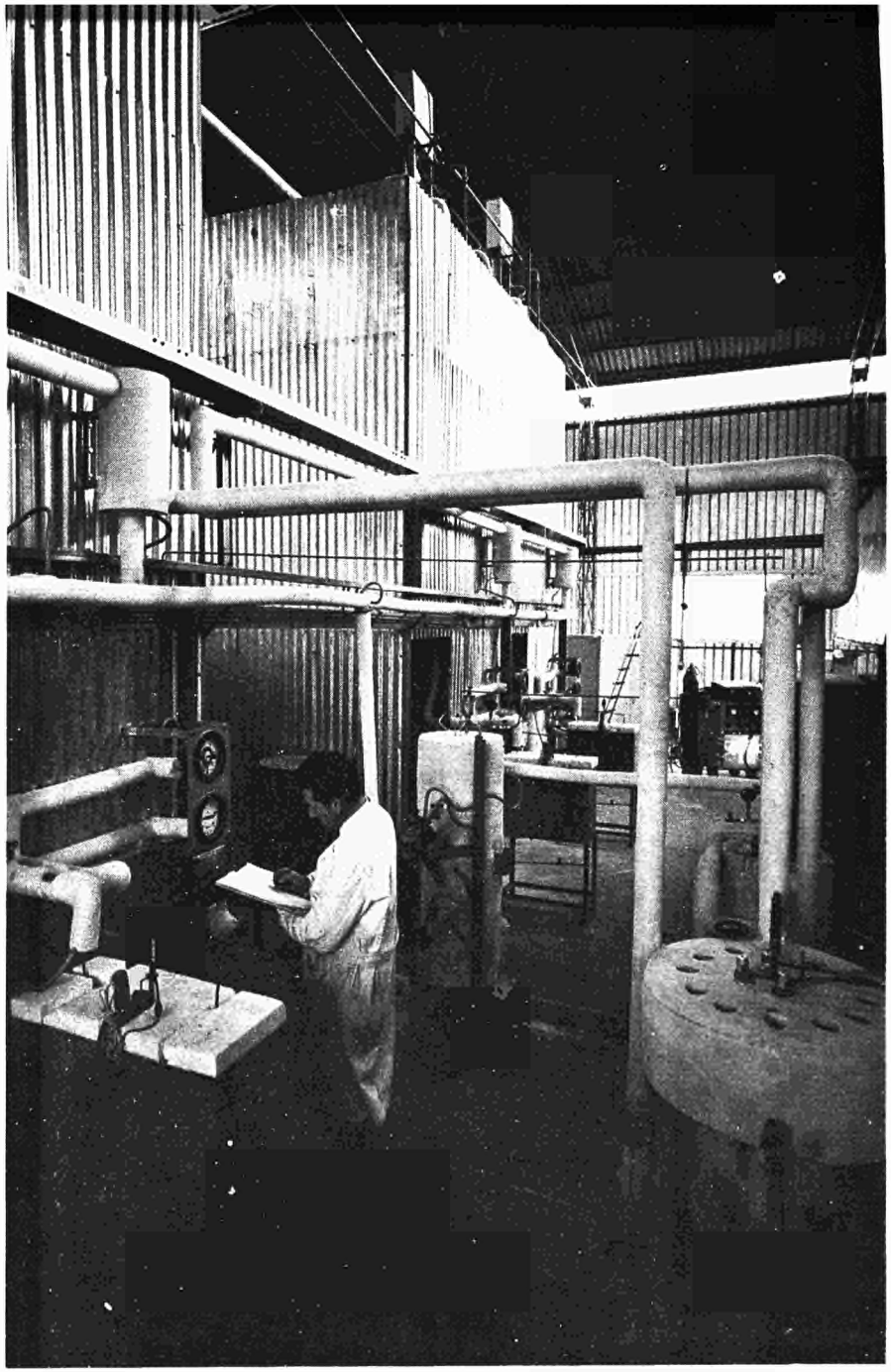


Fig. 3 : General view of a group of four loops

Fig. 4 : View of the control room and control desks

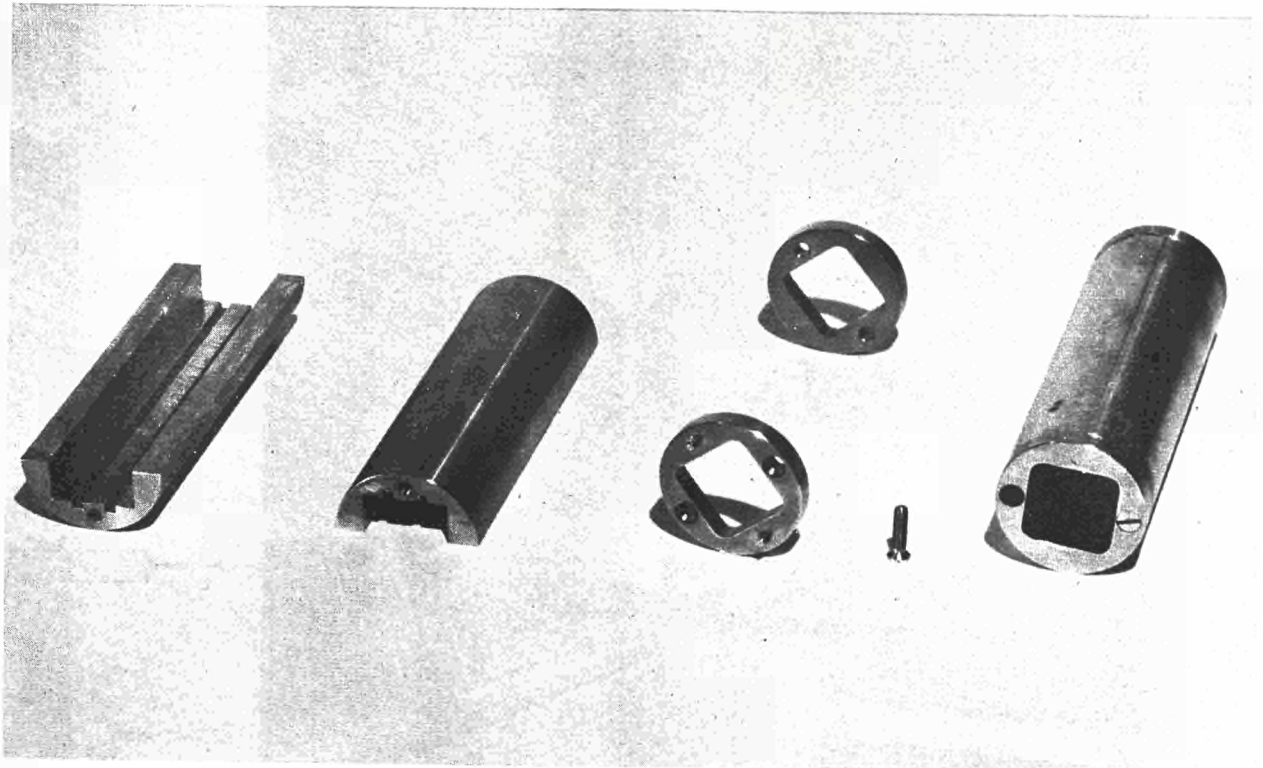


Fig. 5 : Sample holder

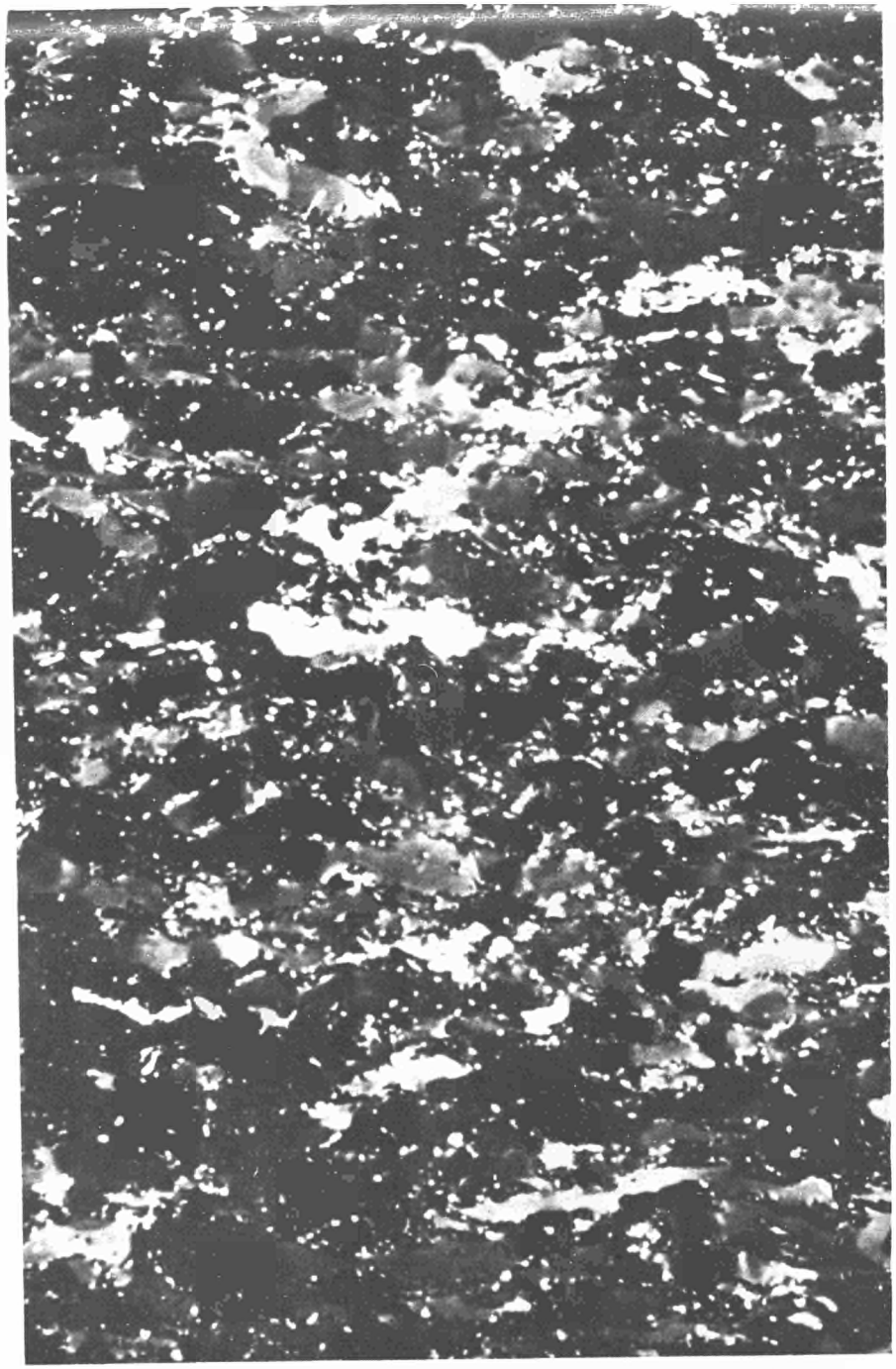


Fig. 6 : Metallography of Zr-3 Nb-1 Sn

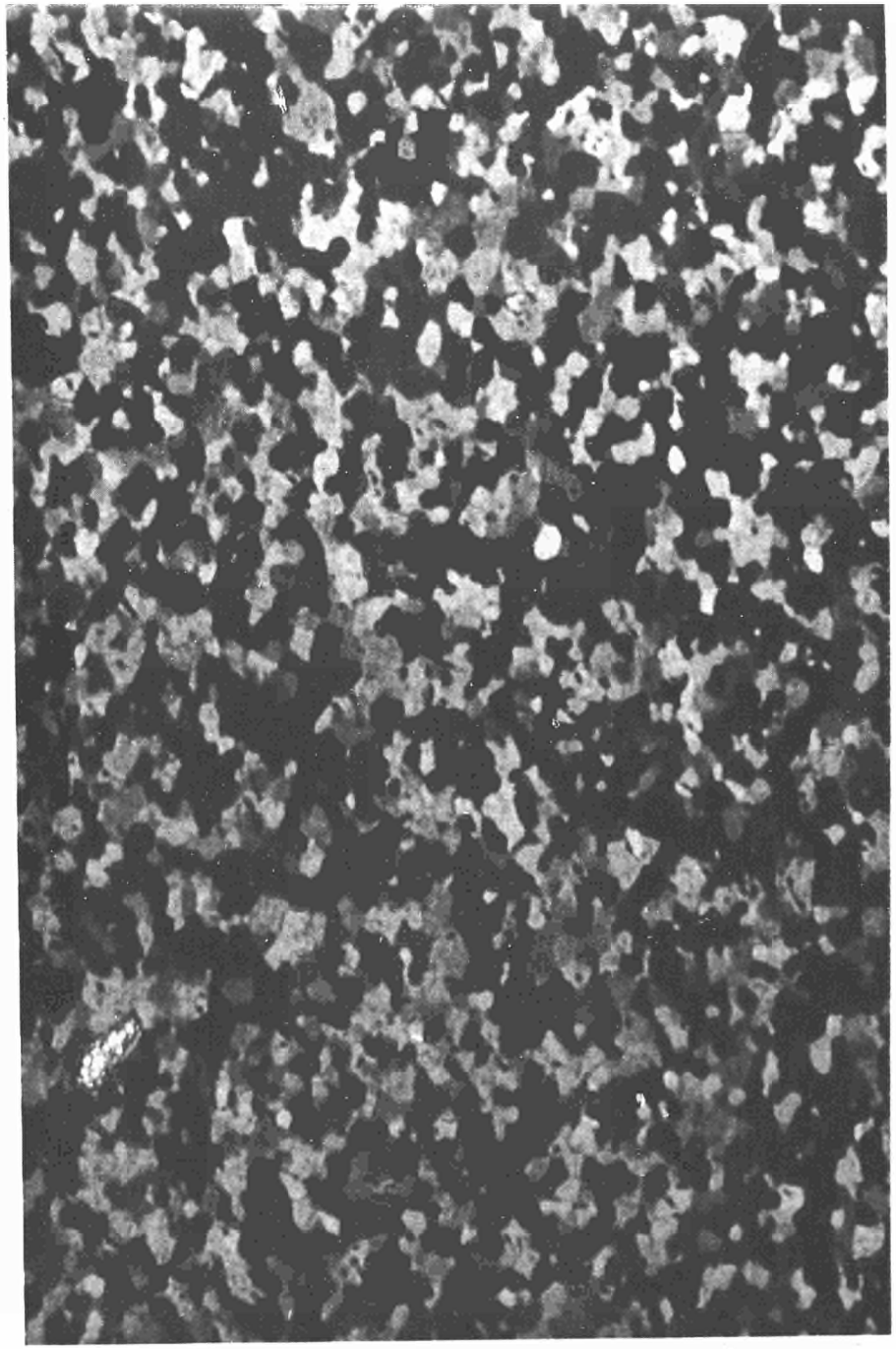


Fig. 7 : Metallography of Zircaloy-2

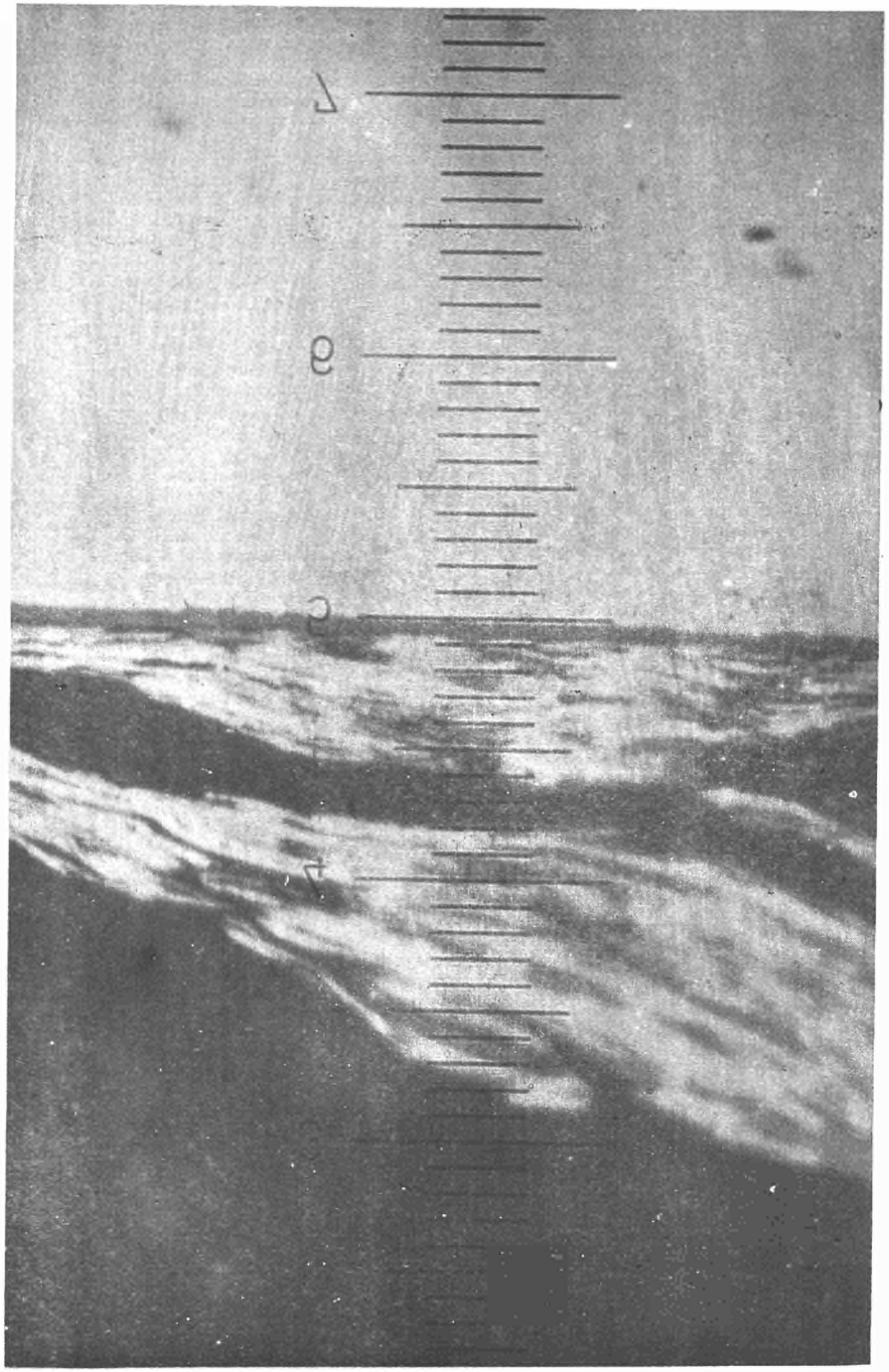


Fig. 8 : Metallography of the oxide layer on Zr-2 corroded at 380°C for 15 days in low chlorine terphenyl.

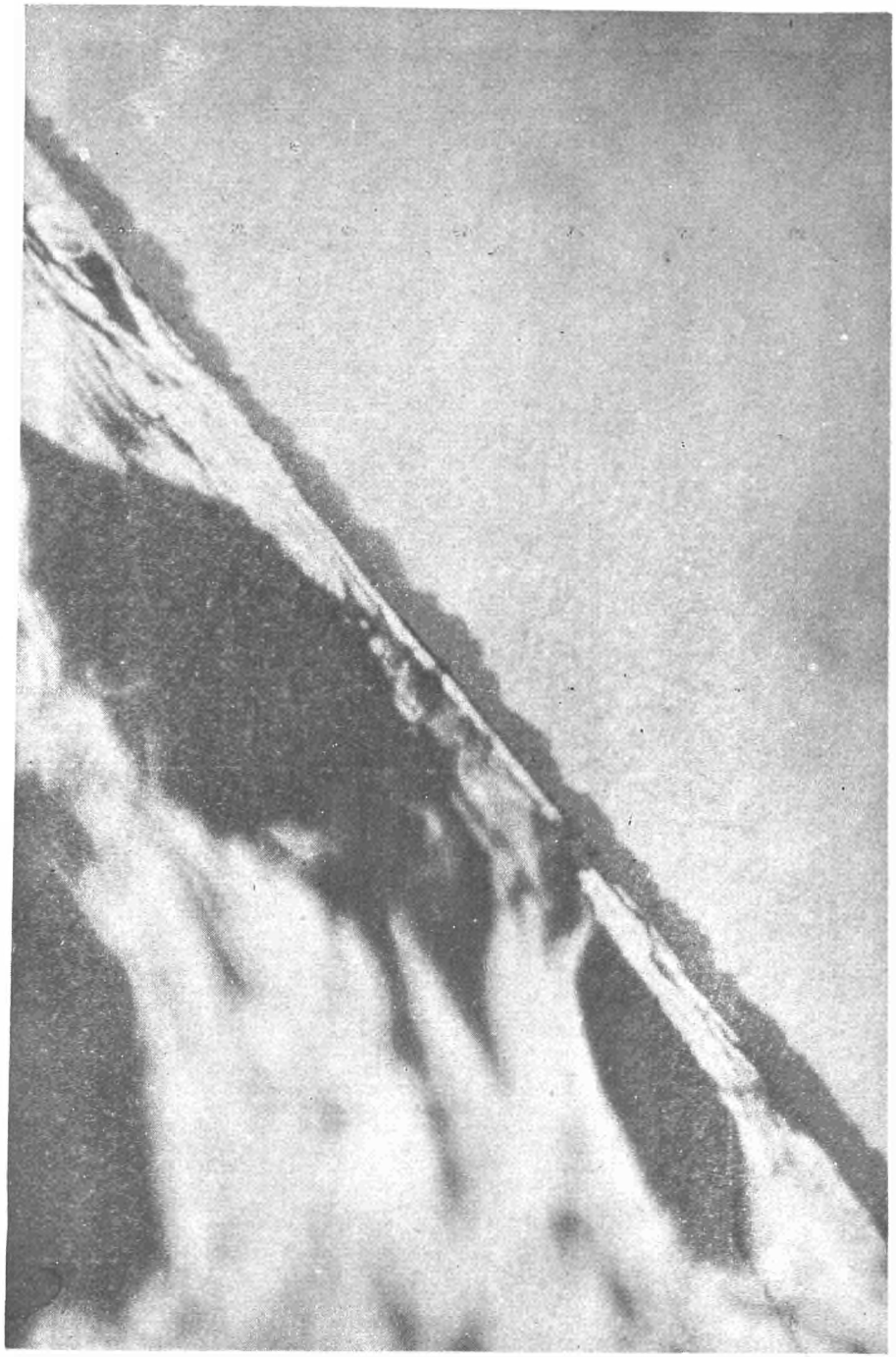


Fig. 9 : Metallography of the oxide layer on Zr-2 corroded at 420°C for 20 days low chlorine.

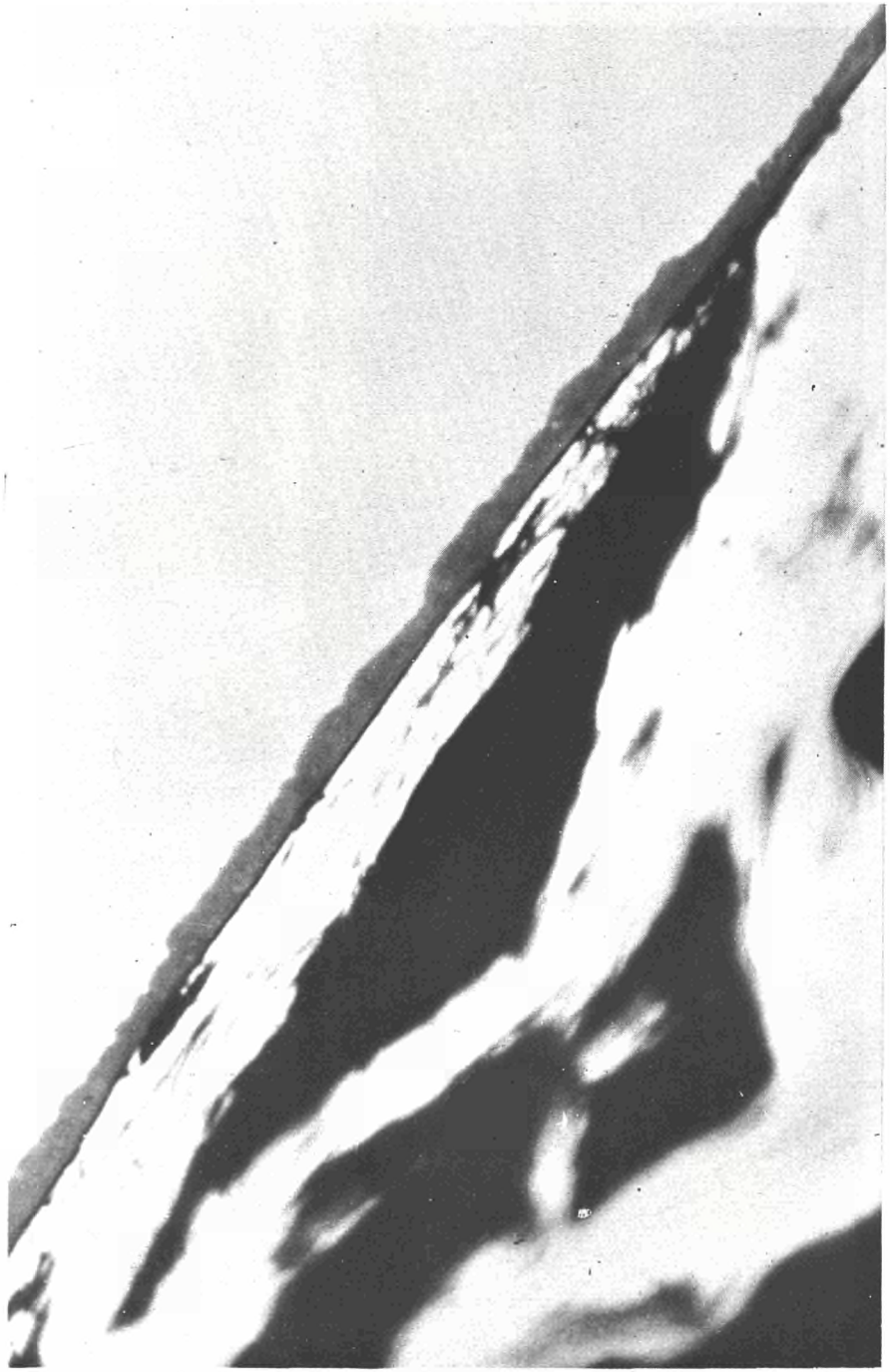


Fig. 10 : Metallography of a different sample in the same conditions of Fig. 9.

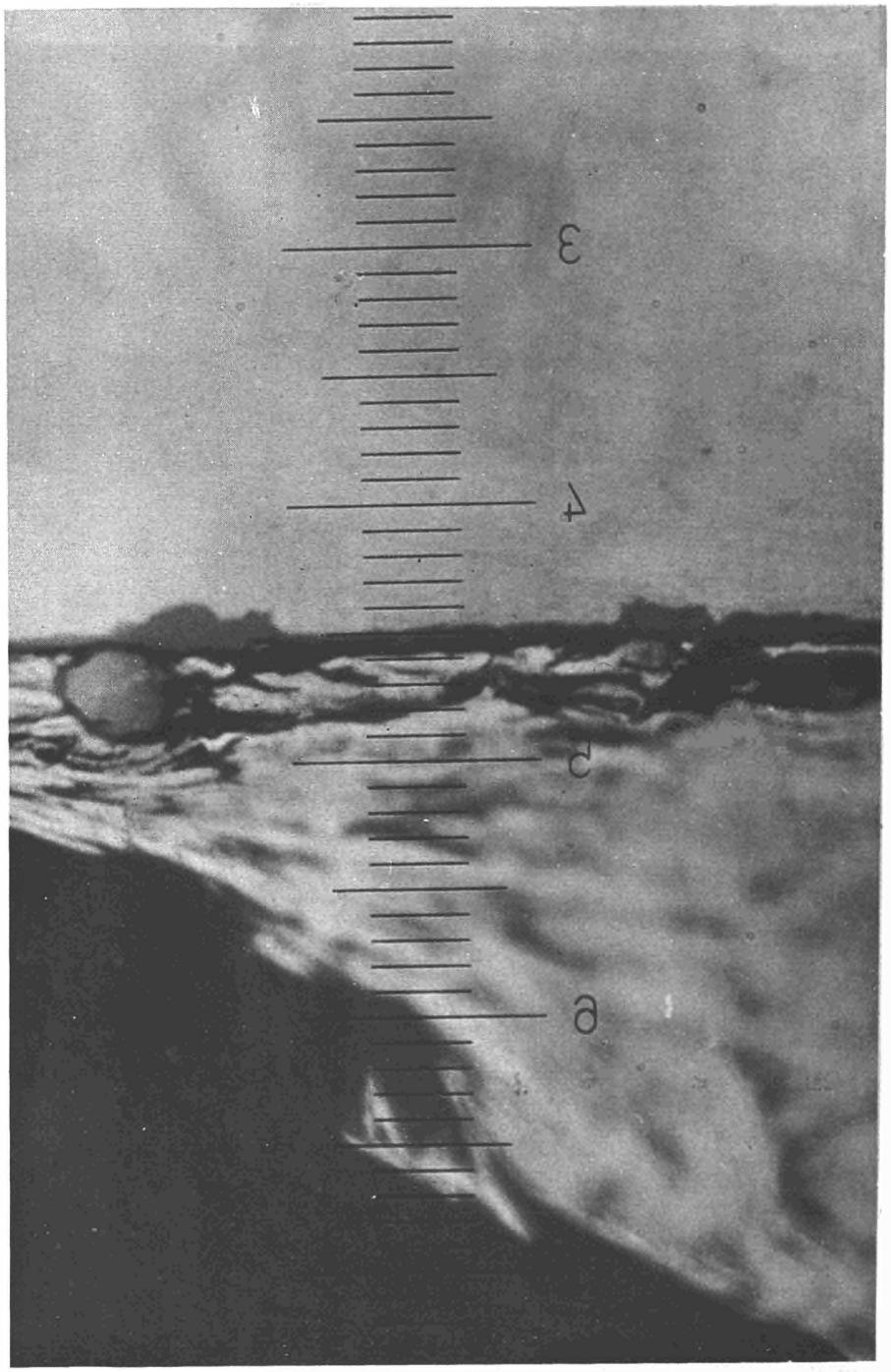


Fig. 11 : Metallography of the oxide layer on Zr-3 Nb-1 Sn corroded at 400°C for 30 days.

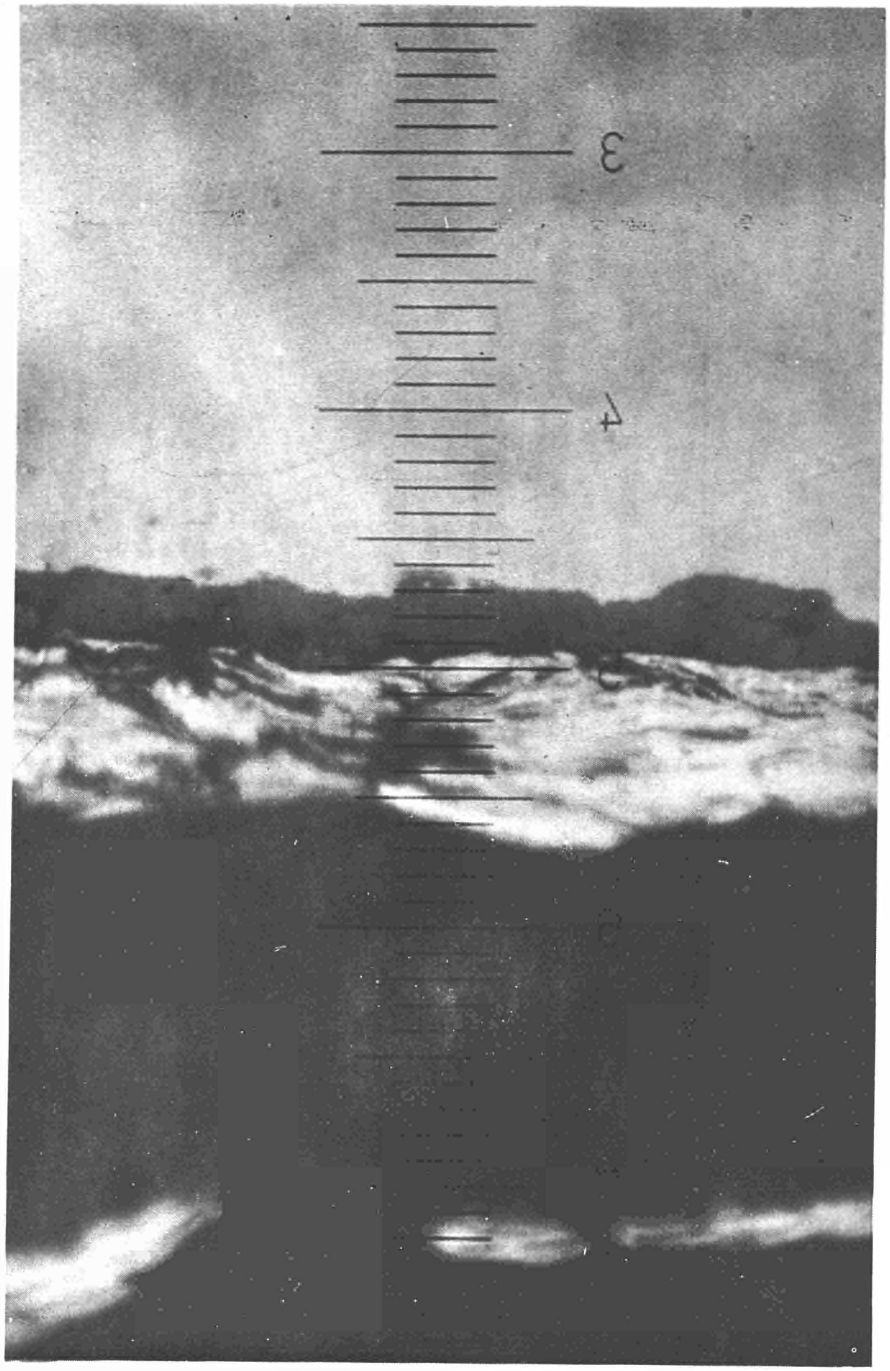


Fig. 12 : Metallography of the oxide layer on Zr-3 Nb-1 Sn corroded at 400 °C for 15 days.

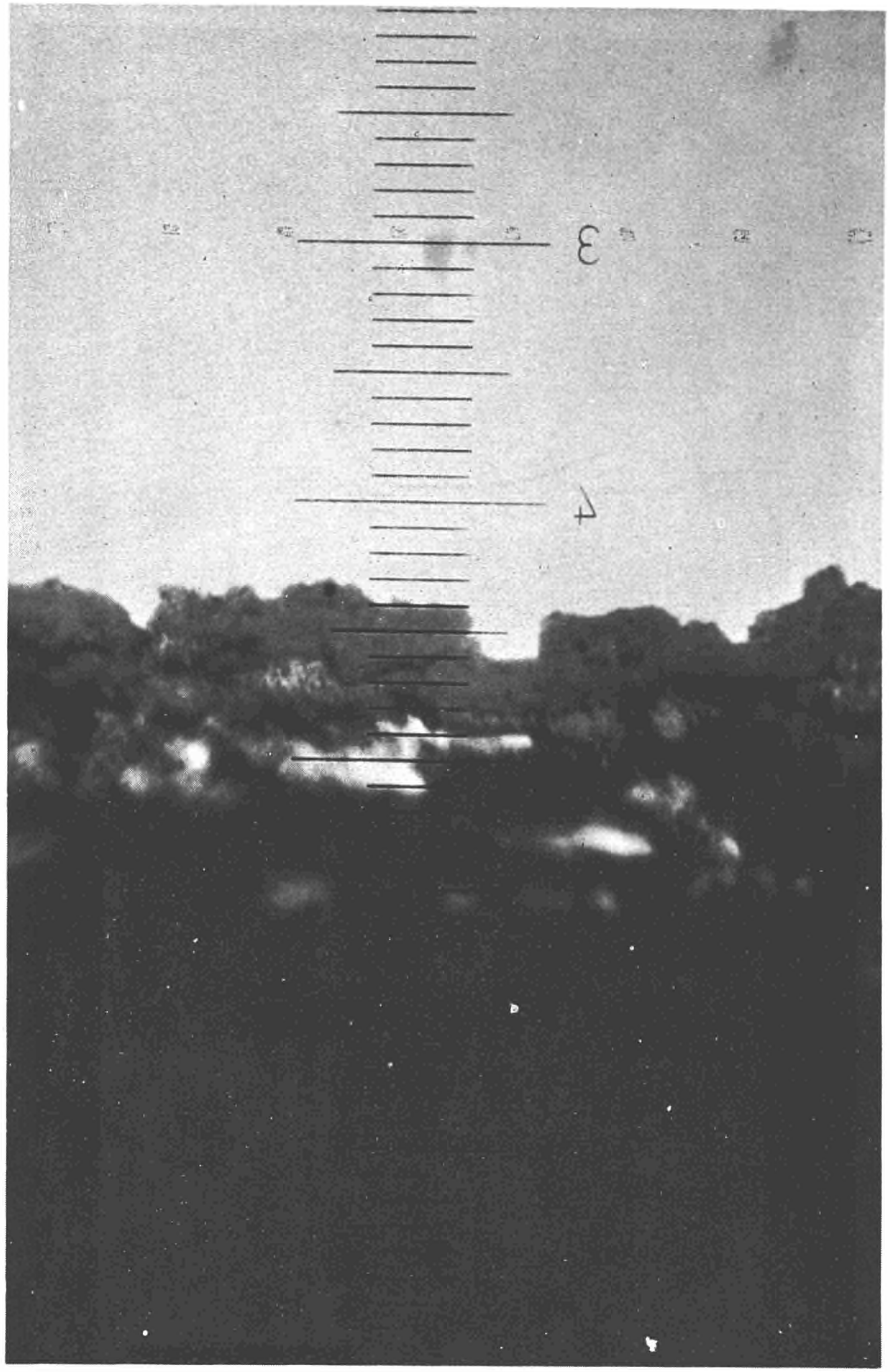
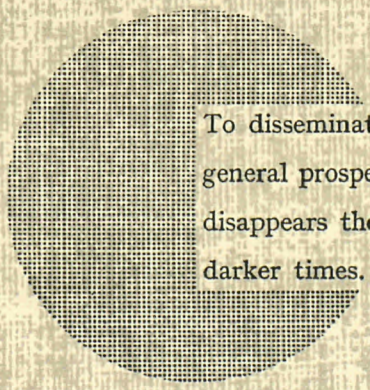


Fig. 13 : Metallography of the oxide layer on Zr-3 Nb-1 Sn corroded at 360 °C für 15 days.



To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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