1957

Influence of some metals on the rate of corrosion and deposition of titanium in molten salt baths

Yu-Pu Huang

Recommended Citation

Huang, Yu-Pu, "Influence of some metals on the rate of corrosion and deposition of titanium in molten salt baths" (1957). *Masters Theses*. 2180.
https://scholarsmine.mst.edu/masters_theses/2180

INFLUENCE OF SOME METALS ON THE RATE OF CORROSION AND DEPOSITION OF TITANIUM IN MOLTEN SALT BATHS

BY

YU-PU HUANG

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1957

Approved by - M. E. Straumanis
Research Professor of Metallurgy

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. M. E. Straumanis, Research Professor of Metallurgy, for his valuable suggestions, guidance, and advice throughout this investigation; to Dr. A. W. Schlechten, Chairman of the Department of Metallurgical Engineering, for his assistance while this work went on.

The author also wishes to express his appreciation to Dr. W. J. James, Associate Professor of Chemistry, for his correction of the manuscript of this thesis.

Table of Contents

List of Tables

List of Figures

I

Introduction

1. History

Titanium is recently gaining great interest in modern industry partially because of its good corrosion resistance in normal atmosphere, humid as well as saline, and to sea water, and nitric acid. These corrosion properties are the same and better than those of stainless steel. As corrosion occurs at the surface of metals, only the surface of the metal has to be corrosion resistant. Such a coating gives resistance just where it is needed instead of making the whole item of stainless steel or titanium. Since stainless steel and titanium are expensive and the former is slowly destroyed by structural corrosion, it seems to be more advantageous to coat cheap metals with titanium, transferring its good corrosion resistance to them. However, the expense of the coating process should be reasonable.

A titanium coating process was developed by the Metallurgy Department of the Missouri School of Mines and Metallurgy and patented in 1955 1). Very few references could be found on titanium coatings before the work was started at the School. The coating process was developed from the study of titanium corrosion phenomena in fused salts 2). It was found that titanium was easily dispersed

---

(1) Gill, C. B., Schlechten, A. W., Straumanis, M. E., "Plating Processes and Depositions", U.S. Patent No. 2,732,321, Jan. 1956.

in fused salts to form a "Pyrosol", and this dispersed titanium could be deposited upon other metals. For example, if a piece of copper sheet was placed in close proximity to a titanium sheet (but not in actual contact) and then the whole was immersed into a fused salt, preferably NaCl or KCl, titanium was transferred to the copper sheet[3]. Later it was found that the process could be improved by putting the base metal to be coated into a mixture of salt with a titanium-oxygen alloy powder and heating the whole above the melting point of the salt in a He atmosphere[4]. By control of the amount of titanium-oxygen alloy powder in the fused salt, and the oxygen content of the powder the method was much improved. The coating experiments lasted for several hours and were performed at 850°C for coatings on copper and at about 1000°C for those on iron and mild steel. It was assumed that by this procedure a diffusion layer was formed by bombardment of the base metal by particles of titanium-oxygen alloy. The thickness of the

---

(2) Gill, C. B., Straumanis, M. E., and Schlechten, A. W., "Corrosion of Titanium in Fused Chlorides", J. Electrochem. Soc., Vol. 102, p. 42, 1955.

(3) Schlechten, A. W., Straumanis, M. E., and Gill, C. B., "Deposition of Titanium Coatings from Pyrosols," J. Electrochem. Soc., Vol. 102, p. 81, 1955.

(4) Shih, S. T., Straumanis, M. E., and Schlechten, A. W., "Deposition of Titanium from Titanium-Oxygen Alloys on Copper, Iron, and Mild Steel," J. Electrochem. Soc., Vol. 103, p. 395, 1956.

coatings depended primarily on temperature and secondly on time, oxygen content of the alloy and the composition of the bath. The coatings obtained looked coherent, nearly free from pits, and they protected the base metal from the attack of nitric acid.

2. The purpose of this investigation

The substances obtained by corrosion of titanium in fused salts, if leached with water and dried, are composed of three kinds of products, namely of black, gray and yellowish ones[5). The black product was identified by X-ray diffraction as titanium-oxygen alloy with 9-10% by weight oxygen which later was used as coating material instead of the titanium sheet for deposition experiments described previously. The yellowish product was identified as rutile. The grayish product was also rutile but containing some titanium powder. Of these three products only the black one possessed the ability to deposit itself upon other metals, forming a titanium diffusion layer. The absolute amount of the corrosion products increased with time of heating and temperature. Since the thickness of titanium diffusion layers depends on the concentration of pyrosols, actually dispersions, in the fused salt the first aim of this research was to collect more information about these dispersions. Thus, the corrosion rates of titanium in fused salts in presence of other metal chlorides were studied in detail because it was suspected that some metal chlorides might increase these rates. The second aim was to investigate the effects on the

---

(5) Chiou, K. C., "Corrosion Products of Titanium in Fused Salt Baths," Master's Thesis, Missouri School of Mines and Metallurgy, 1954.

formation of titanium coatings by precoating the base metal with other metals. Corrosion tests, to check the quality of the coatings were also made.

II

Material, Equipment and Experimental Procedure

1. Material used in this research

The titanium used was produced by Remington Arms Company in form of a rolled sheet 1.5 mm thick (nominal purity over 99 per cent). The material was previously analyzed by the hydrogen evolutions method 6), and it was found to contain 97.5% by weight of titanium.

All the chemicals used were of reagent, of U.S.P. or at least of C.P. grades.

2. Small resistance furnace

The corrosion experiments in molten NaCl were carried out in air. In a second series of experiments the air was replaced by helium.

The salt was melted in small crucibles, which were placed in a small resistance furnace. The latter consisted of an alundum core, 50 mm in diameter, 60 mm high, around which and the bottom a nickel-chromium resistance wire was wound. The core was placed in a hole carved in porous insulating ceramic bricks. The temperature of the core was automatically controlled by a Honeywell-Pyr-o-vane device, connected with a chromel-alumel thermocouple.

A small crucible containing 30 grams of a salt mixture (NaCl and one other metal salt) was put into this furnace, and heated to 900°C.

---

(6) Straumanis, M. E., Chen, P. C., "The Mechanism and Rate of Dissolution of Titanium in Hydrofluoric Acid," J. Electrochem. Soc., Vol. 98, p. 234, 1951.

Titanium samples (about 0.8 cm x 2.2 cm) were first weighed and then they were submerged in the molten salt bath mentioned above. They were left there for one hour and then were cooled together with the salt bath and the furnace. To remove and examine the titanium samples, the salt was dissolved in boiling water, the samples were washed with cold water, cleaned with a soft brush, dried and weighed. Thus the percentage weight loss and the rate of corrosion could be calculated. The corrosion products, insoluble in water, were collected and separated by decantation into light and heavy fractions. Attempts were made to identify the composition of the residues by X-ray diffraction.

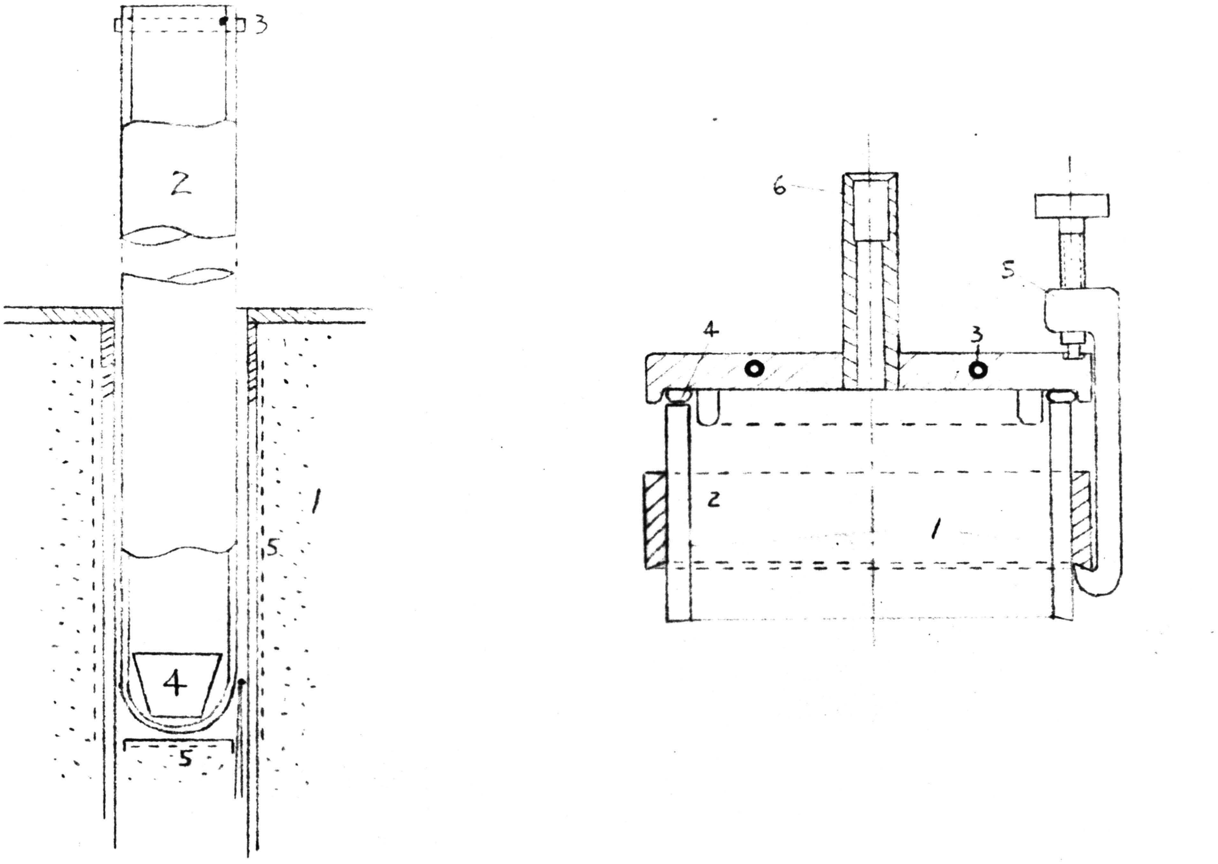
Different amounts of metal salts other than NaCl were added to the sodium chloride, namely 0.5, 1, 2, 5 per cent by weight in a dry state.

3. Vacuum type drying furnace

The salts for experiments carried out in presence of helium were used in a dry form to avoid the complications caused by water vapor. The well ground salts were placed in small crucibles and pushed into the oven. Then the latter was evacuated and the temperature was slowly raised. The maximum temperature that could be reached and which was automatically maintained was 125°C. The salts were dried at 106°C and then cooled in vacuum. The oven was made by the Precision Scientific Company. Both combined and free water were driven off very well.

4. The helium atmosphere electric resistance furnace

The second series of titanium corrosion experiments were performed in an inert atmosphere. The electric resistance furnace, as shown in Fig. 1, consisted of a thermally insulated alundum core around which the resistance wire was wound.



Furnace

1. furnace body
2. porcelain tube
3. steel ring
4. big crucible
5. Ni-Cr resistant wire

Furnace Cap

1. porcelain tube
2. steel ring
3. water cooling
4. O-ring
5. clamp
6. joint to vacuum pumping system

Figure 1. - The helium atmosphere electric resistance furnace and furnace cap.

A porcelain tube, 90 mm in diameter and 900 mm long, which could be evacuated, was inserted in the core of the furnace. While the lower part of the tube could be heated, the upper part was exposed to air and was provided with a cap to make connection with the vacuum pump system.

Each run consisted of four samples of different composition of salt mixture. A big crucible, 85 mm in diameter, 80 mm high, was used to hold four small crucibles, embedded in aluminium oxide powder (Fig. 2), to minimize the danger of spilling the salt during handling. Fig. 2 shows the arrangement of the crucibles in detail.

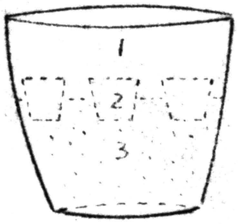


Figure 2. - Position of small crucibles.

1. **big crucible**
2. **small crucible**
3. **aluminum oxide powder**

After the samples (as shown by Fig. 2) were in the furnace, the mullite tube of the furnace was covered with a cap and evacuated with the aid of a vacuum pump. The pumping system was connected to a source of dry purified helium so that the furnace could be filled with helium after the evacuation of air. The helium filled in the furnace was pumped out and refilled two more times to be sure that only traces of oxygen remained in the mullite tube. After the power was turned on, the gas pressure in the tube of the furnace was held a few centimeters above atmospheric to prevent possible ingress of air.

A further difference between the procedure in the small (open to the air) and big furnace was as follows: in the former the titanium samples were submerged into the molten salts when the salts had just melted while in the latter the titanium samples were embedded in the dry salt mixtures, and gradually heated by raising the temperature to 900°C and higher. Other procedures, such as weighing, separating, etc. were the same.

5. The X-ray camera and the sample mounting

For the X-ray investigation of the corrosion products obtained, a small X-ray powder camera 6.4 cm in diameter was used for making the powder patterns. The sample mount was prepared as follows:

The washed and dried corrosion products were ground in a mortar until they became very fine. This fine powder was caused to adhere uniformly to a thin glass hair, having a diameter of 0.08 mm and precoated with a small amount of a non-drying glue 7). The diameter of the finished sample including the glass hair was about 0.15 mm. The finished specimen was centered under a microscope, so that the sample mount located in the camera would rotate exactly in the central axis of the camera during the time of exposure by X-rays.

---

(7) Straumanis, M. E., J. Appl. Phys., Vol. 20, p. 726, 1946.

An X-ray film of 3 x 18 cm was inserted in the camera in an asymmetric manner[7] which has the following advantages if a thin specimen and a precision camera is used:

(1) The specimen is exactly centered to coincide with the axis of the camera, therefore, the error due to lack of centering is greatly minimized.

(2) Both front reflection and back reflection lines are simultaneously registered on the same film.

(3) The sample for the X-ray pattern is made in such a manner that the error due to absorption by the sample is negligible, if lines in the higher back reflection region are used for calculation of the lattice constant.

(4) No standard substances are necessary.

The X-ray patterns of the corrosion products were made for identification purposes to compare them subsequently with various X-ray patterns of materials of known composition. The selection and preparation of materials with known composition was made on the basis of what composition the possible corrosion products might have.

III

Experimental Results

1. The influence of metal salt additions on the corrosion rate of titanium in fused NaCl.

Twenty kinds of metal salts, listed in Table I were tried out in presence of air. Among them, only a few, namely $FeCl_3$, $NiCl_2$, $CoCl_2$, $CdCl_2$, CuCl were found to increase the rate of the titanium corrosion reaction. The others produced only a layer of some precipitate on the titanium samples which probably hindered the rate of corrosion. The next step in this investigation was to determine these rates.

Table I

Metal salts which were used as additions to NaCl

Effective	Ineffective
$FeCl_3 \cdot 6H_2O$	$ZrOCl_2$
CuCl	$MnCl_2 \cdot 4H_2O$
$NiCl_2 \cdot 6H_2O$	$SrCl_2 \cdot 6H_2O$
$CoCl_2 \cdot 6H_2O$	VCl_3
$CdCl_2 \cdot 2H_2O$	$NdCl_3$
	TlCl
	$CrCl_3 \cdot 6H_2O$
	$BaCl_2 \cdot 2H_2O$
	$AlCl_3$
	$SnCl_2 \cdot 2H_2O$
	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$
	$Mg(C_2H_3O_2)_2 \cdot 4H_2O$
	$Tl(C_2H_3O_2)$
	$BeCO_3$
	$AgNO_3$
	$ZnSO_4$

2. Rates of corrosion of titanium as caused by various concentration of heavy metal salts added to NaCl in presence of air.

The rate of corrosion was calculated by the following formula:

$$V = \frac{x - x_1}{(t_1 - t)A} = \frac{\Delta x}{A \Delta t} \qquad (I)$$

where V represents the rate of corrosion, x is the initial weight of the titanium sample at time t, and x_1 is the weight of the corroded sample at time t_1. Since the weight loss Δx increases with time $\frac{\Delta x}{\Delta t}$ is positive. A is the corroding surface area of the titanium sample.

However, as titanium metal will undergo an exchange reaction with the more noble metal salts, it was necessary to consider the influence of the exchange reaction on the corrosion of titanium. The exchange reaction may be as follows, for instance, in case of CuCl

$$\begin{aligned} & \mathrm{Ti} + 3\ \mathrm{CuCl} \longrightarrow 3\ \mathrm{Cu} + \mathrm{TiCl_3} \\ \text{or}\quad & \mathrm{Ti} + 2\ \mathrm{CuCl} \longrightarrow 2\ \mathrm{Cu} + \mathrm{TiCl_2} \end{aligned} \qquad \text{(II)}$$

The lower titanium chlorides decompose at 900°C as follows:8)

$$\begin{aligned} & 3\ \mathrm{TiCl_2} \longrightarrow \mathrm{Ti} + 2\ \mathrm{TiCl_3} \\ \text{or}\quad & 4\ \mathrm{TiCl_2} \longrightarrow \mathrm{Ti} + 3\ \mathrm{TiCl_4} \end{aligned} \qquad \text{(III)}$$

The $TiCl_4$ escaped from the bath in form of dense white vapors.

The weight loss because of reaction (II) had to be subtracted from the total weight loss caused by both reactions, the corrosion reaction and reaction (II). For example, the weight loss of a titanium sample due to corrosion in 1% CuCl-NaCl salt mixture in presence of air at 900°C for one hour was obtained as follows:

One gram of CuCl will require, according to reaction (II), $\frac{47.9}{297.09} = 0.161$ g of titanium to form $TiCl_3$. The weight of CuCl in the 1% salt mixture (30 g) was 30 x 1% = 0.3 g. It was found

---

(8) Straumanis, M. E., Shih, S. T., and Schlechten, A. W., "The Mechanism of Deposition of Titanium Coatings from Fused Salt Bath," J. Electrochem. Soc., Vol. 104, p. 17, 1957.

that the total weight loss of the titanium sample after corrosion for one hour at 900°C was 0.405 g. The loss due to corrosion alone was therefore:

$$0.405 - 0.3 \times 0.161 = 0.357 \text{ grams of titanium}$$

The sample had a total surface area of 5.14 cm^2. The rate of corrosion, V (in mg/cm^2 hr) was then calculated by equation (I):

$$V = \frac{357}{5.14 \times 1} = 69.4 \text{ mg/cm}^2 \text{ hr}$$

The corrosion loss (in %) was also calculated by dividing the weight lost due to corrosion with the weight of the sample before corrosion. For example, the weight loss due to corrosion alone in the 1% CuCl experiment in presence of air at 900°C for one hour was 0.357 grams and the weight of the same sample before corrosion was 1.450 grams, so that the corrosion loss was:

$$\frac{0.35}{1.45} \times 100 = 24.6\%$$

The experimental results showing the influence of the addition of the five salts (see Table I) on the rate of corrosion of titanium in presence of air in fused NaCl are summarized in Tables II, III, IV, V, and VI.

Table II

Corrosion losses and rates of corrosion of titanium samples in presence of air in fused NaCl containing CuCl

Addition CuCl in % by wt.	Wt. before corrosion mg	Total Wt. loss mg	Wt. loss due to corrosion mg	Surface area of sample cm^2	Corrosion loss in %	Corrosion rate mg/cm^2 hr
0.5	1700	335	311	5.89	18.3	52.7
1	1450	405	357	5.14	24.6	69.4
2	1390	615	518	4.96	37.3	104.5
5	1570	1075	833	5.50	53.1	151.4

Table III

Corrosion losses and rates of corrosion of titanium samples in presence of air in fused NaCl containing $CoCl_2$

Addition $CoCl_2$ in % by wt.	Wt. before corrosion mg	Total Wt. loss mg	Wt. loss due to corrosion mg	Surface area of sample cm^2	Corrosion loss in %	Corrosion rate mg/ cm^2 hr
0.5	1555	350	313	5.46	20.1	57.4
1	1365	485	411	4.88	30.1	84.2
2	1320	715	567	4.75	43.0	119.5
5	1450	1195	826	5.14	57.0	160.7

Table IV

Corrosion losses and rates of corrosion of titanium samples in presence of air in fused NaCl containing $NiCl_2$

Addition $NiCl_2$ in % by wt.	Wt. before corrosion mg	Total Wt. loss mg	Wt. loss due to corrosion mg	Surface area of sample cm^2	Corrosion loss in %	Corrosion rate mg/ cm^2 hr
0.5	1510	25	0		0	0
1	1600	390	316	5.59	19.8	54.7
2	1415	570	422	5.04	29.8	83.8
5	1500	670	300	5.29	20.0	56.8

Table V

Corrosion losses and rates of corrosion of titanium samples in presence of air in fused NaCl containing $CdCl_2$

Addition $CdCl_2$ in % by wt.	Wt. before corrosion mg	Total Wt. loss mg	Wt. loss due to corrosion mg	Surface area of sample cm^2	Corrosion loss in %	Corrosion rate mg/ cm^2 hr
0.5	1600	275	249	5.59	15.6	44.5
1	1415	380	328	5.04	23.2	65.1
2	1455	600	496	5.16	34.1	96.1
5	1525	1290	1029	5.37	67.4	191.7

Table VI

Corrosion losses and rates of corrosion of titanium samples in presence of air in fused NaCl containing $FeCl_3$

Addition $FeCl_3$ in % by wt.	Wt. before corrosion mg	Total Wt. loss mg	Wt. loss due to corrosion mg	Surface area of sample cm^2	Corrosion loss in %	Corrosion rate mg/cm^2hr
0.5	565	60	16	2.47	2.8	6.4
1	775	245	157	3.10	20.2	50.4
2	665	310	133	2.77	20.0	48.0
5	1470	765	323	5.20	21.9	62.0

3. Rates of corrosion of titanium as caused by various concentrations of heavy metal salts added to NaCl in presence of helium.

The experiments carried out in helium were performed in six different concentrations for each heavy metal salt. The results are given in Tables VII, VIII, IX, X, and XI.

Table VII

Corrosion losses and rates of corrosion of titanium samples in presence of helium in fused NaCl containing CuCl

Addition CuCl in % by wt.	Wt. before corrosion mg	Total Wt. loss mg	Wt. loss due to corrosion mg	Surface area of sample cm^2	Corrosion loss in %	Corrosion rate mg/cm^2hr
0.5	120	65	57	3.54	6.2	16.1
1	815	140	124	3.22	15.2	38.4
2	910	255	223	3.51	24.5	63.5
3	1015	340	292	3.83	28.7	76.2
4	1325	485	421	4.76	31.7	88.3
5	1005	505	424	3.80	42.2	111.8

Table VIII

Corrosion losses and rates of corrosion of titanium samples in presence of helium in fused NaCl containing $CoCl_2$

Addition $CoCl_2$ in % by wt.	Wt. before corrosion mg	Total Wt. loss mg	Wt. loss due to corrosion mg	Surface area of sample cm^2	Corrosion loss in %	Corrosion rate mg/cm^2hr
0.5	1062.9	103.0	90.7	3.97	8.5	22.8
1	924.7	112.7	88.1	3.55	9.5	24.8
2	1037.1	210.4	161.4	3.89	15.6	41.4
3	1076.7	261.0	187.3	4.01	17.4	46.7
4	1159.1	385.0	286.7	2.26	24.7	67.3
5	1227.0	483.3	360.4	4.47	29.4	80.7

Table IX

Corrosion losses and rates of corrosion of titanium samples in presence of helium in fused NaCl containing $NiCl_2$

Addition $NiCl_2$ in % by wt.	Wt. before corrosion mg	Total Wt. loss mg	Wt. loss due to corrosion mg	Surface area of sample cm^2	Corrosion loss in %	Corrosion rate mg/cm^2hr
1	610	85	60	2.60	9.9	23.2
2	485	70	21	2.23	4.3	9.3
3	650	125	51	2.73	7.9	18.7
4	650	220	122	2.73	18.7	44.6
5	650	280	157	2.73	24.1	57.6

Table X

Corrosion losses and rates of corrosion of titanium samples in presence of helium in fused NaCl containing $CdCl_2$

Addition $CdCl_2$ in % by wt.	Wt. before corrosion mg	Total Wt. loss mg	Wt. loss due to corrosion mg	Surface area of sample cm^2	Corrosion loss in %	Corrosion rate mg/cm^2hr
0.5	475	65	56	2.20	11.9	25.6
1	475	80	63	2.20	13.2	28.5
2	545	115	80	2.41	14.7	33.3
3	580	220	168	2.51	28.9	66.8
4	640	270	200	2.69	31.3	74.4
5	675	330	243	2.80	36.0	86.8

Table XI

Corrosion losses and rates of corrosion of titanium samples in presence of helium in fused NaCl containing $FeCl_3$

Addition $FeCl_3$ in % by wt.	Wt. before corrosion mg	Total Wt. loss mg	Wt. loss due to corrosion mg	Surface area of sample cm^2	Corrosion loss in %	Corrosion rate mg/ cm^2hr
0.5	385	40	25	1.92	6.6	13.1
1	485	35	6	2.23	1.1	2.5
2	460	90	31	2.15	6.7	14.4
3	590	105	17	2.54	2.8	6.5
4	595	130	12	2.56	2.0	4.7
5	580	155	8	2.51	1.3	3.0

4. Rates of corrosion of titanium in fused NaCl without any additions of heavy metal salt in presence of helium.

For the purpose of comparison two experiments were carried out in helium with fused NaCl in which no addition of heavy metal salt was made. An average value of rate of corrosion was obtained as 0.22 mg/cm^2 hr. The results are given in Table XII.

Table XII

Corrosion losses and rates of corrosion of titanium samples in presence of helium in fused NaCl without addition of any heavy metal salt

Experiment No.	Sample No.	Corroding time hr.	Wt. before corrosion mg	Wt. loss due to corrosion mg	Surface area of sample cm^2	Corrosion loss in %	Corrosion rate mg/ cm^2hr	Ave. Corrosion rate mg/ cm^2hr
1	1	1	879.0	0	3.4	0	0	
1	2	1	921.1	1.3	3.3	0.14	0.39	
1	3	1	942.6	0.8	3.6	0.08	0.22	0.23
1	4	1	797.8	1.0	3.3	0.13	0.30	
2	1	4	943.5	4.7	3.6	0.50	0.33	
2	2	4	878.1	0.2	3.4	0.02	0.01	0.22
2	3	4	856.9	3.4	3.4	0.40	0.25	
2	4	4	953.0	4.1	3.6	0.43	0.28	

IV

Titanium Coating Experiments

1. Experimental procedure.

The titanium coating experiments were carried out in the large resistance furnace in a helium atmosphere. The procedure described previously for corrosion experiments was modified so that the heating temperature, e.i., coating temperature was 1000°C for three hours. The charges were composed of ingot iron plates submerged in 10 grams of a mixture of NaCl and titanium powder containing some oxygen (TiO_x). The ingot iron plates were cut from a rolled bar, 1/2 inch in diameter, from which the scale had been removed on the lathe, and both sides of the plates were polished. The plating mixture in all experiments consisted of 10% TiO_x and 90% NaCl. However, titanium powder of two different oxygen contents, namely 8 and 15 at % (99 and 94wt%) was used for this investigation.

The polished ingot iron plates were then put into aqueous solutions of more noble metal salts in order to produce a thin layer of the noble metals on them. It was expected that this layer might facilitate the deposition of titanium later in the fused salt bath.

For the production of the surface layer the solution of $CuSO_4$, $NiSO_4$, $AgNO_3$, $CoSO_4$, $AuCl_3$, $PtCl_4$, $CdSO_4$, $SnCl_2$, and $Pb(NO_3)_2$ (from 1 to 10 normal) were chosen. The polished ingot iron plates were first immersed for a while into a small test tube (about 15 min. in $AgNO_3$, 2 min. in $CuSO_4$) filled with an aqueous solution of the respective metal salt, and then, after draining off the solution, were carefully washed with distilled water. The precoated and washed plates were slowly dried on a small drying plate. The deposition reaction is a displacement reaction occurring for instance in $CuSO_4$ according to:

$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu$ (deposited upon the iron plate) (IV)

The precoated, washed and dried ingot iron plates were weighed after drying. Since the weight changes due to reaction (IV) were very small, no attempt was made to calculate the weight lost or gained by the plates due to corrosion and deposition according to this reaction.

For each experiment four ingot iron plates were used, of which three were dipped into the same metal salt aqueous solutions for the same length of time so that the amount of metal deposited was approximately the same. The fourth plate, with no deposit on it, served as a sample for comparison. All four plates were then embedded in the NaCl-TiO_x mixture, heated under helium and treated further as already described in the corrosion experiments.

The coated samples were tested for the completeness of the coating by immersing them into a solution of $CuSO_4$. It is known that in case of a sound titanium coating there will be no deposition of copper upon the sample 9). However, if there are pores in the coating, copper will be deposited on these spots according to reaction (IV). Thus red spots on the Ti-coatings testify to the bad quality of the coating.

---

(9) Shih, S. T., Straumanis, M. E., and Schlechten, A. W., "Deposition of Titanium from Titanium-Oxygen Alloys on Copper, Iron, and Mild Steel," J. Electrochem. Soc., Vol. 103, p. 395, 1954.

2. Weight of coatings.

The coated ingot iron plates were weighed after the leaching and drying operations, so that the increase in weight could be stated, as the weight of the plate with the thin coating of the noble metal on it was already known. The weight gained, divided by the total surface of ingot iron sample, expressed in mg/cm^2 represents the condition of coating on the sample, and the figures can be used for comparison. However, as the fluctuations in weight of the coating from experiment to experiment were appreciable, there was no other possibility to compare the quality (weight) of the coatings obtained under different conditions, but the statistical approach. Thus, a series of titanium coating experiments of samples precoated with Cu, Ni, Ag, Au, Pt was made and the average of each series was used for comparison with each other and with the not precoated samples. Since all of the four samples of each experiment were exactly under the same experimental conditions, the results obtained seemed to be quite reliable and comparable with other experimental series. The results are shown in Tables XIII-XVIII, with samples precoated with Cu (Table XIII), Ag (Table XIV), Ni (Table XV), Au (Table XVI) and Pt (Table XVII). The experiments which did not show any improvement after precoating the plates with various other metals like Co, Pb, Cd and Sn are listed in Table XVIII.

Some of the ingot iron samples were provided with a second titanium coating and some of them were coated with a heavier titanium layer from NaCl both containing 20% of TiO$_x$ which contained 15 at % of oxygen (94% by wt.) at a temperature of 1000°C (Tables XIX and XXII).

Table XIII

Weight of titanium coatings deposited on ingot iron plates, precoated and not precoated with Cu.

Ti on Cu-precoated iron samples.					Ti on pure iron samples.				
Ex. No.	Total Wt. increase mg	Weight increase mg/cm^2	Average wt. increase mg/cm^2	Test in $CuSO_4$	Ex. No.	Total Wt. increase mg	Weight increase mg/cm^2	Test in $CuSO_4$	Remarks
6-4	32.1	8.448	8.448	No spots	6-1	16.5	4.581	red spots	1. Ex. 10-1 was not used to count for the total average figure.
7-1	23.1	6.016	6.016	No spots	7-4	17.5	4.946	No spots	
10-1	23.9	6.124	6.124	No spots					
11-1	33.5	8.764	8.764	No spots	11-4	27.5	7.569	No spots	
14-1	18.9	5.170		No spots	14-4	18.8	5.136	No spots	
14-2	18.9	4.982	5.053	No spots					2. All experiments were carried out with TiO_x containing 8 at % oxygen.
14-3	19.0	5.006		No spots					
16-1	20.6	5.756		No spots	16-4	22.0	6.221	No spots	
16-2	22.1	6.273	5.817	No spots					
16-3	18.9	5.421		No spots					
17-1	27.7	7.492		red spots	17-4	20.5	5.595	red spots	
17-2	25.2	7.010	7.197	red spots					
17-3	25.2	7.089		No spots					
19-1	20.7	5.837		red spots	19-4	20.5	5.527	red spots	
19-2	20.1	5.788	6.386	No spots					
19-3	28.1	7.534		red spots					
20-1	21.5	6.180		No spots	20-4	16.7	4.883	red spots	
20-2	21.2	5.869	5.752	No spots					
20-3	20.1	5.208		No spots					
Total Average			6.679	79% showed no red spots			5.557	50% showed no red spots	

Table XIV

Weight of titanium coatings deposited on ingot iron plates, precoated and not precoated with Ag.

Ti on Ag-precoated iron samples.					Ti on pure iron samples.				
Ex. No.	Total Wt. increase mg	Weight increase mg/cm^2	Average wt. increase mg/cm^2	Test in $CuSO_4$	Ex. No.	Total Wt. increase mg	Weight increase mg/cm^2	Test in $CuSO_4$	Remarks
8-1	31.9	8.464	7.504	No spots	8-4	22.8	6.544	No spots	1. All experiments were carried out with TiO_x containing 8 at % oxygen.
8-2	23.7	6.543		red spots					
11-2	23.2	9.015	8.531	No spots	11-4	27.5	7.569	No spots	
11-3	27.7	8.047		No spots					
21-1	20.4	5.541	5.514	No spots	21-4	15.2	4.126	No spots	
21-2	17.8	5.725		No spots					
21-3	22.9	6.275		No spots					
22-1	17.2	5.113	5.119	red spots	22-5	17.9	5.305	No spots	
22-2	17.0	5.012		No spots					
22-3	19.4	5.700		No spots					
22-4	15.4	4.650		No spots					
23-1	26.2	7.776	7.348	No spots	23-5	25.5	7.180	No spots	
23-2	31.1	8.747		No spots					
23-3	21.5	6.323		No spots					
23-4	22.2	6.546		No spots					
26-1	18.4	5.664	5.575	No spots	26-4	15.8	4.746	No spots	
26-2	18.4	5.424		No spots					
26-3	19.6	5.637		No spots					
	Total Average		6.599	89% showed no red spots			5.911	100% showed no red spots	

Table XV

Weight of titanium coatings deposited on ingot iron plates, precoated and not precoated with Ni.

Ti on Ni-precoated iron samples.					Ti on pure iron samples.				
Ex. No.	Total Wt. increase mg	Weight increase mg/cm^2	Average Wt. increase mg/cm^2	Test in $CuSO_4$	Ex. No.	Total Wt. increase mg	Weight increase mg/cm^2	Test in $CuSO_4$	Remarks
7-2	23.7	6.158	6.158	No spots	7-4	17.5	4.946	red spots	1. All experiments were carried out with TiO_x containing 8 at % oxygen.
12-1	27.5	6.868		red spots	12-4	25.4	7.010	No spots	
12-2	24.0	6.669	6.591	No spots					
12-3	25.0	6.236		No spots					
13-1	22.4	5.521		No spots	13-4	18.7	4.766	No spots	
13-2	19.7	5.311	5.263	No spots					
13-3	19.3	4.957		No spots					
15-1	18.8	5.611		No spots	15-4	19.0	5.286	No spots	
15-2	21.4	5.803	5.939	No spots					
15-3	24.1	6.402		No spots					
18-1	29.4	8.016	7.041	No spots	18-3	28.5	7.712	No spots	
18-2	22.8	6.066		red spots					
	Total Average		6.199	83.3% showed no red spots			5.944	80% showed no red spots	

Table XVI

Weight of titanium coatings deposited on ingot iron plates, precoated and not precoated with Au.

Ti on Au-precoated iron samples.					Ti on pure iron samples.				
Ex. No.	Total Wt. increase mg	Weight increase mg/cm^2	Average Wt. increase mg/cm^2	Test in $CuSO_4$	Ex. No.	Total Wt. increase mg	Weight increase mg/cm^2	Test in $CuSO_4$	Remarks
27-1	21.2	6.440	6.136	No spots	27-4	21.5	6.507	No spots	1. Ex. No. 27-1, 27-2, 27-3, 27-4 were carried out with TiO_x containing 8 at % oxygen.
27-2	23.7	6.952		No spots					
27-3	15.9	5.016		No spots					
30-2	25.1	7.214	7.214	No spots	30-4	21.1	6.195	No spots	
31-1	22.4	5.540	5.540	No spots	31-4	24.1	5.955	No spots	
32-2	41.0	10.503	10.302	No spots	32-4	40.2	10.405	No spots	
32-3	38.6	10.101		No spots					2. Ex. No. 31-1, 31-4, 32-2, 32-3, 32-4 were carried out with TiO_x containing 15 at % oxygen.
	Total Average		7.298	100% showed no red spots			7.266	100% showed no red spots.	

Table XVII

Weight of titanium coatings deposited on ingot iron plates, precoated and not precoated with Pt.

Ti on Pt-precoated iron samples.					Ti on pure iron samples.				
Ex. No.	Total Wt. increase mg	Weight increase mg/cm^2	Average Wt. increase mg/cm^2	Test in CuSO$_4$	Ex. No.	Total Wt. increase mg	Weight increase mg/cm^2	Test in CuSO$_4$	Remarks
28-1	20.5	5.592	5.309	No spots	28-4	19.0	5.312	No spots	1. Ex. No. 28-1, 28-2, 28-3, 28-4, were carried out with TiO$_x$ containing 8 at % oxygen.
28-2	17.6	5.847		No spots					
28-3	19.6	5.487		No spots					
30-1	26.0	7.124	7.124	No spots	30-4	21.1	6.195	No spots	
31-2	24.5	6.207	6.338	No spots	31-4	24.1	5.955	No spots	
31-3	26.3	6.469		No spots					
32-1	41.0	11.144	11.144	No spots	32-4	40.2	10.405	No spots	
Total Average			7.481	100% showed no red spots			6.967	100% showed no red spots	2. Ex. No. 30-1, 30-4, 31-2, 31-3, 31-4, 32-1, 32-4 were carried out with TiO$_x$ containing 15 at % oxygen.

Table XVIII

Weight of titanium coatings deposited on ingot iron plates, precoated and not precoated with several metals which gave no improvement.

Ex. No.	Metal pre-coated	Total Wt. increase mg	Weight increase mg/cm^2	Average Wt. increase mg/cm^2	Test in $CuSO_4$	Ex. No.	Total Wt. increase mg	Weight increase mg/cm^2	Test in $CuSO_4$	Remarks
8-3	Co	19.7	5.432	5.432	No spots	8-4	22.8	6.544	No spots	1. All experiments were carried out with TiO_x containing 8 at % oxygen.
9-3	Co	17.7	4.682	4.682	No spots	9-4	18.1	4.666	No spots	
24-1	Co	16.0	4.938		No spots	24-4	21.3	6.455	No spots	
24-2	Co	21.1	6.251	5.681	No spots					
24-3	Co	19.2	5.853		No spots					
	Total Average		5.159		100% showed no red spots			5.885	100% showed no red spots	
29-1	Pb	14.1	4.333		red spots	29-4	15.9	4.917	No spots	
29-2	Pb	12.8	5.238	4.835	No spots					
29-3	Pb	17.4	4.933		No spots					
30-3	Pb	19.6	5.543	5.543	No spots	30-4	21.1	6.195	No spots	
	Total Average			5.189	75% showed no red spots			5.556	100% showed no red spots	
9-2	Cd	16.2	4.396	4.396	red spots	9-4	18.1	4.666	No spots	
9-1	Sn	17.4	4.594	4.594	No spots	9-4	18.1	4.666	No spots	

3. Corrosion properties of titanium coatings.

The titanium coatings usually consist of an outer layer and of several intermediate layers[10]. The thickness of the whole coating depends on time and temperature of coating[11]. The outer layer is of high metallic titanium content showing a more or less crystalline appearance depending on time and temperature of coating. At shorter coating times and lower temperatures the crystalline structure of the titanium layer did not show up. The intermediate layer consists of about 50/50 at. % Fe-Ti phase[12]. Then follows a diffusion layer of Ti in Fe. As metallic titanium processes good corrosion resistance against the action of HNO_3, dilute solution of HCl, H_2SO_4 and of sea water, one should expect that the corrosion resistance of titanium-coated samples be similar. In this investigation solutions of 1 N HNO_3, 1/20 N H_2SO_4, 1/20 N HCl, and of 2% NaCl were used as corrosion agents. The experiment was performed as follows: Into a small beaker of 50 mm

---

(10) M. E. Straumanis, and A. W. Schlechten, "Titan-Überzuge auf Metallen und Keramischen Objekten," Metall, 10, p. 901-909, 1956.

(11) Shih, S. T., Straumanis, M. E., and Schlechten, A. W., "Deposition of Titanium from Titanium-Oxygen Alloys on Coppers, Iron, and Mild Steel," J. Electrochem. Soc., Vol. 103, p. 395, 1954.

(12) Straumanis, M. E. and Schlechten, A. W., "Titan-Überzüge auf Metallen und Keramischen Objekten," Metall, 10, p. 901-909, 1956.

diameter and 60 mm height containing 50 c.c. of corrosion agent was inserted a coated sample. The beaker was covered with a watch glass. After every 24 hours this coated sample was taken out, washed, dried, the surface examined under a microscope, weighed, and put back into the same corrosion agent.

All these samples were found to decrease in weight and some holes on the surfaces of the samples were observed under the microscope. A closer examination of the Ti-coated iron samples showed that the coatings were not corroded at all but the iron was attacked by these solutions through the few pores in the Ti-coatings. Thus the coatings at the pore locations were partially undermined. The best of all these Ti-coated samples was one precoated with Au. It withstood the action of the H_2SO_4 solution 4 days. Thereafter a faster corrosion started, evidently the acid found its way to the iron through some pores in the coating.

So the result was that of 44 coated samples which produced no copper spots in a $CuSO_4$ aqueous solution, none was found possessing good corrosion resistance in an acid or a NaCl solution.

4. The production of thick titanium layers in recoating experiments.

All these experiments described above showed clearly that a single titanium coating has some pores through which the base metal can easily be attacked by corrosion agents. So an attempt was made to seal these pores by producing a thicker titanium layer by recoating. The respective experiments were carried out with six ingot iron plates. Two of them were precoated with copper, two with silver (see page), and the rest was bare for comparison. The plates were embedded in a salt mixture consisting of 15% TiO_x

(of 15 at % oxygen) and 85% NaCl. The three crucibles, each containing two samples, were placed in a large crucible and were heated under helium at 1000°C for one hour. After leaching the salt and cleaning the samples, the respective plates were immersed in $CuSO_4$ and $AgNO_3$ solution to deposit copper or silver on the irons through the possible pores in the titanium coatings. The samples treated in this way were coated the second time at 1000°C for 3 hours. Table XIX shows the weight of coatings of these recoated samples. The weight of all these samples increased. Two out of six samples (a bare plate and a silver precoated one) had very good corrosion resistance in 2% NaCl aqueous solution, as no change in weight occurred after three months of immersion.

In the next series of the recoating experiments the samples were slightly scratched with a knife after the first coatings (for three hours) to expose the uncovered pores and to remove all the big lumpy and loose TiO_x masses sticking to the surface of the titanium coatings. Care was taken not to cause cracks in the titanium layer. Then the loose fragments on the samples were removed by flushing with water. To decide which of the precoating metals worked best, a run consisting of eight samples prepared by this procedure was made. The results, as shown in Table XX, were that all of the three Ag-precoated samples did not show any corrosion in 2% NaCl aqueous solution as compared to none of two Cu-precoated and three bare iron plates.

Table XIX

Weight of titanium coatings of recoating experiments.

		First Coating		Second Coating		Total		
Ex. No.	Precoated with	Weight increase mg/cm^2	Average Wt. increase mg/cm^2	Weight increase mg/cm^2	Average Wt. increase mg/cm^2	Total Wt. increase mg/cm^2	Average total wt. increase mg/cm^2	Remarks
33-1	Cu	4.764	5.155	12.861	13.170	17.625	18.325	1. First coating was obtained in a melt of containing TiO$_x$ (15 at % oxygen) at 1000° in 1 hr. 2. Second in a melt containing TiO$_x$ 15 at % oxygen, 1000°C 3 hrs. 3. 15% TiO$_x$ was used.
33-2	Cu	5.547		13.478		19.025		
33-3	Ag	5.022	4.843	10.494	10.854	15.516	15.697	
33-4	Ag	4.664		11.214		15.878		
33-5	bare	4.076	3.896	11.366	10.416	15.442	14.312	
33-6	bare	3.717		9.466		13.182		

Table XX

Comparison of titanium coatings obtained on Ag-precoated, Cu-precoated, and on bare iron in modified titanizing process (Scratching slightly the first titanium coatings).

Ex. No.	Precoated with	1st Ti coating. Weight* increase mg/cm^2	Test in $CuSO_4$	2nd Ti coating. Weight increase mg/cm^2	Total wt. increase mg/cm^2	Test in 2% NaCl solution
35-1	Ag	8.914	No red spots	9.180	18.094	No yellow spots
35-2	Ag	7.793	No red spots	8.001	15.794	No yellow spots
35-3	Ag	10.530	No red spots	9.326	19.856	No yellow spots
35-4	Cn	7.790	No red spots	10.034	17.824	yellow spots
35-5	Cn	6.869	red spots	8.037	14.906	yellow spots
35-6	bare	5.424	red spots	7.583	13.007	yellow spots
35-7	bare	5.794	red spots	6.897	12.691	yellow spots
35-8	bare	4.794	red spots	6.773	11.567	yellow spots

Remarks: * After scratching
First coating was obtained at 1000°C in 3 hrs (15% by wt. TiO_x, 8 at % oxygen).
Second coating, repeating the same operation.

A further experiment was also made with Ag-precoated samples to show the advantage obtained in weight increase of titanium coatings by a second immersion into $AgNO_3$ solution after slight scratching,washing as described above in the recoating process. The results are shown in Table XXI.

One more attempt was made to obtain thick titanium layers by using more TiO_x in the molten salt mixture. It was performed with 20% TiO_x and 80% NaCl. Table XXII shows the results. The coatings obtained were porous and rough. All of the six samples corroded in NaCl solution.

Table XXI

Comparison of weight increases of titanium coatings on samples immersed into $AgNO_3$ solution after slightly scratching the first titanium coatings.

Ex. No.	Titanium weight increase in mg/cm^2			Sample Treatment
	First Coating	Second Coating	Total	
36-1	8.875	8.482	17.357	immersed into $AgNO_3$ aqueous solution after slightly scratching
36-2	8.108	9.849	17.957	
36-3	8.153	8.333	16.486	
Average	8.379	8.888	17.267	
36-4	8.140	7.636	15.776	no second immersion
36-5	7.660	7.685	15.345	
Average	7.900	7.661	15.561	

Remark: First coating was obtained at 1000° in 3 hrs. (15 % by wt. TiO_x, 8 at % oxygen).
Second coating: repeating the same operation.

Table XXII

Weight of titanium coatings obtained in a melt containing large amounts of TiO_x.

Ex. No.	Precoated with	Total weight increase mg	Weight increase mg/cm^2	Average Wt. increase mg/cm^2	Remarks
34-1	Cu	97.5	24.983	23.708	1. Bath composition: 20% TiO_x,(containing 85 at % Ti, 15 at % oxygen), 80% NaCl.
34-2	Cu	89.6	22.433		
34-3	Ag	71.2	17.370	17.373	
34-4	Ag	66.5	17.375		
34-5	bare	67.2	17.147	17.895	
34-6	bare	70.3	18.648		2. Coating temperature: 1000°C.
					3. Coating time: 3 hrs.

V

Discussion

1. Corrosion phenomena of titanium in fused salts in presence of air and helium.

Figures 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 were based on the data as given in Tables II, III, IV, V, and VI. The figures show that both the corrosion rate and the percentage loss increased in the presence of air. The rate of corrosion increased also with the concentration of the more noble metal salts added to the NaCl. Among the 20 salts tried out in the addition experiments, only 5 accelerated the rate of corrosion appreciably. These salts in the sequence of decreasing activity are: $CdCl_2$, $CoCl_2$, CuCl, $NiCl_2$ and $FeCl_3$. The other salts were nearly inactive or decreased the corrosion rate in presence of air. In the case of the active additions, the rate of corrosion in presence of air was higher than in helium. Usually the rate increased with the concentration of the heavy metal salt in the bath along a straight line which was always correct in case of corrosion under helium. In presence of air the increase occurred also along a curve and in one case ($NiCl_2$ additions) the formation of a maximum at about 2% $NiCl_2$ was observed. In case of $FeCl_3$ additions the rate of corrosion slowly decreased with the concentrations of the additions in experiments performed under helium.

The five straight lines representing the rate of corrosion under helium are shown in Fig. 3, Fig. 5, Fig. 7, Fig. 9, and Fig. 11. The curve obtained with $NiCl_2$ is shown in Fig. 7, and the corrosion behavior of titanium in presence of $FeCl_3$ is shown in

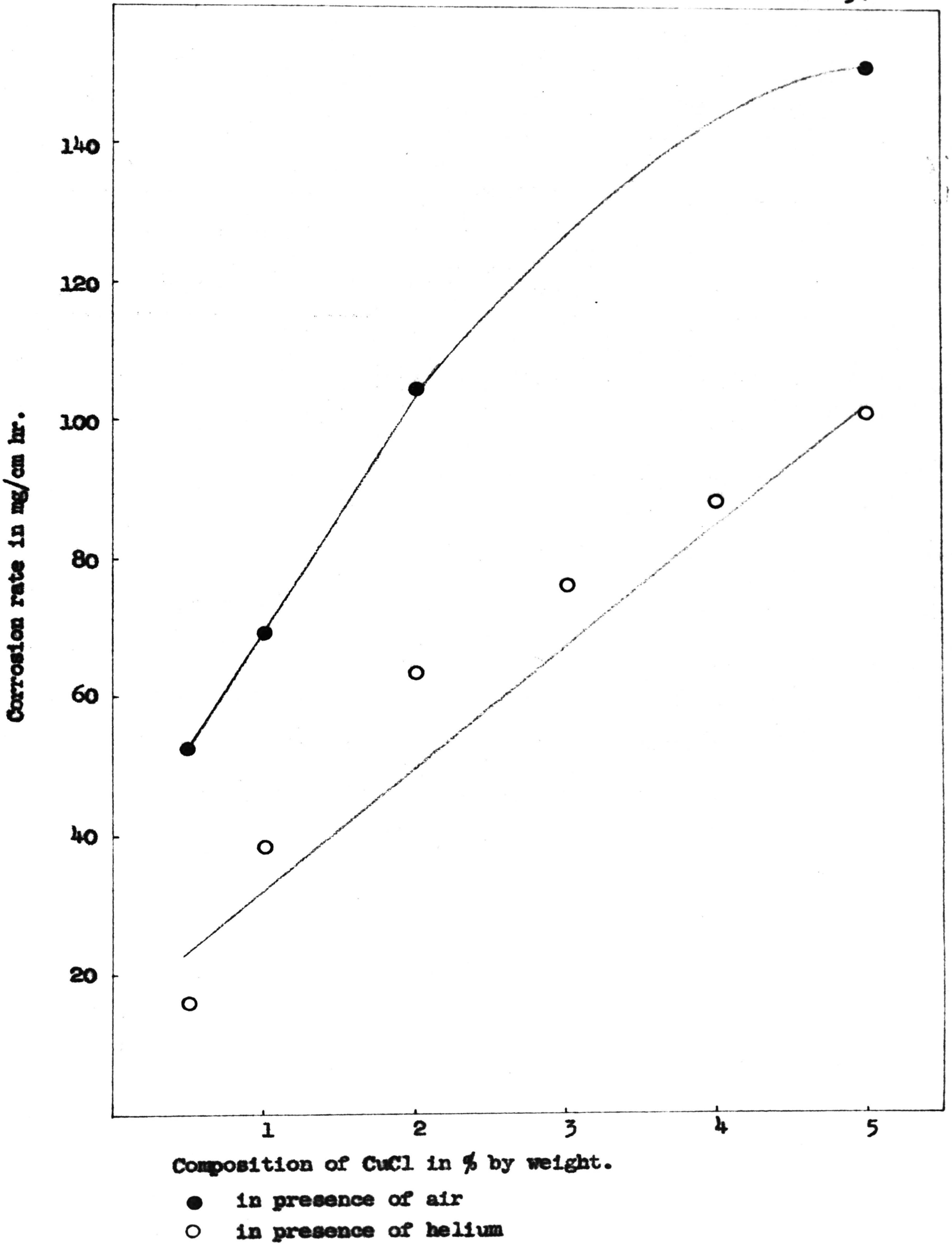


Figure 3. - Corrosion rate of titanium in fused NaCl containing CuCl.

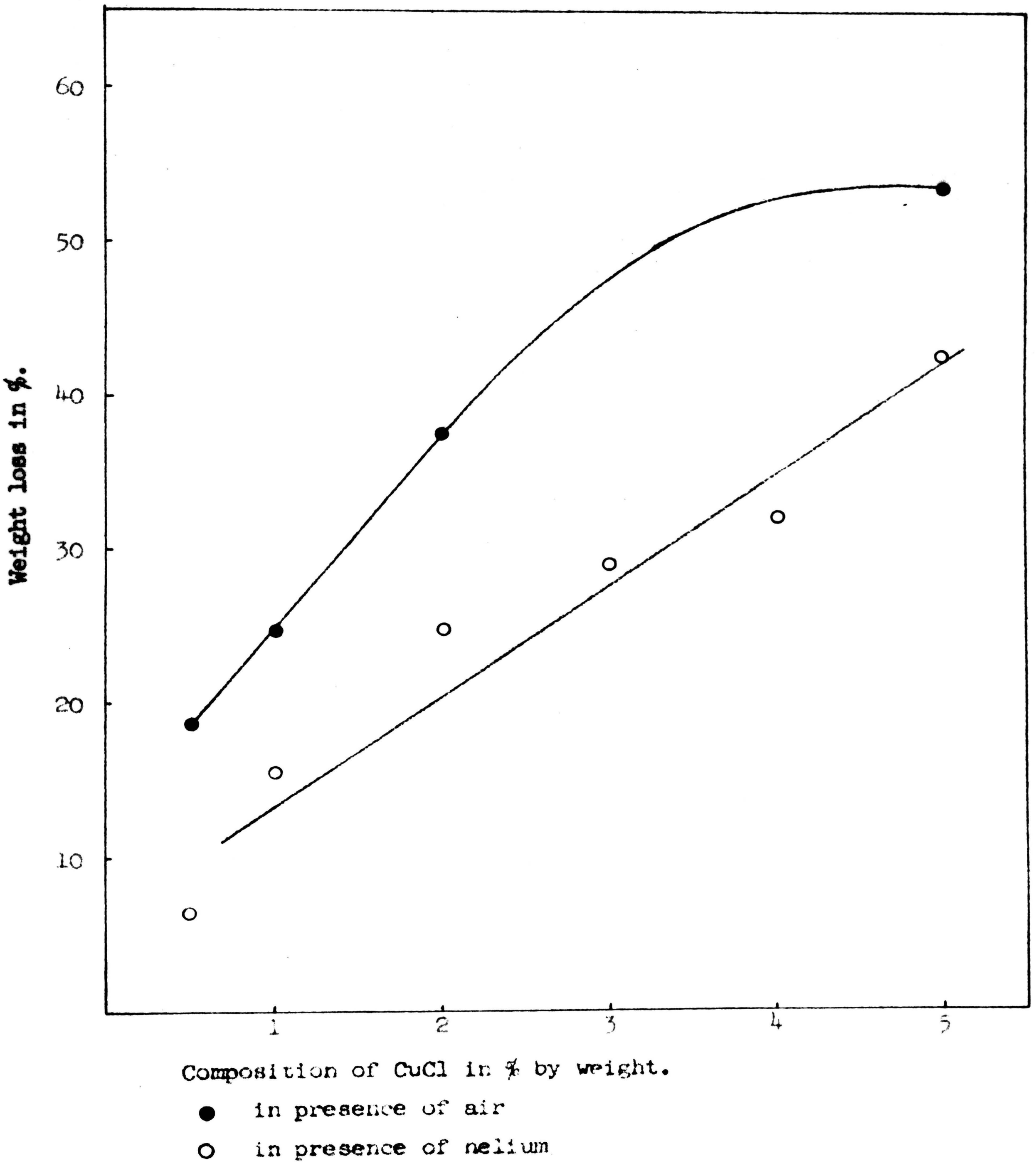
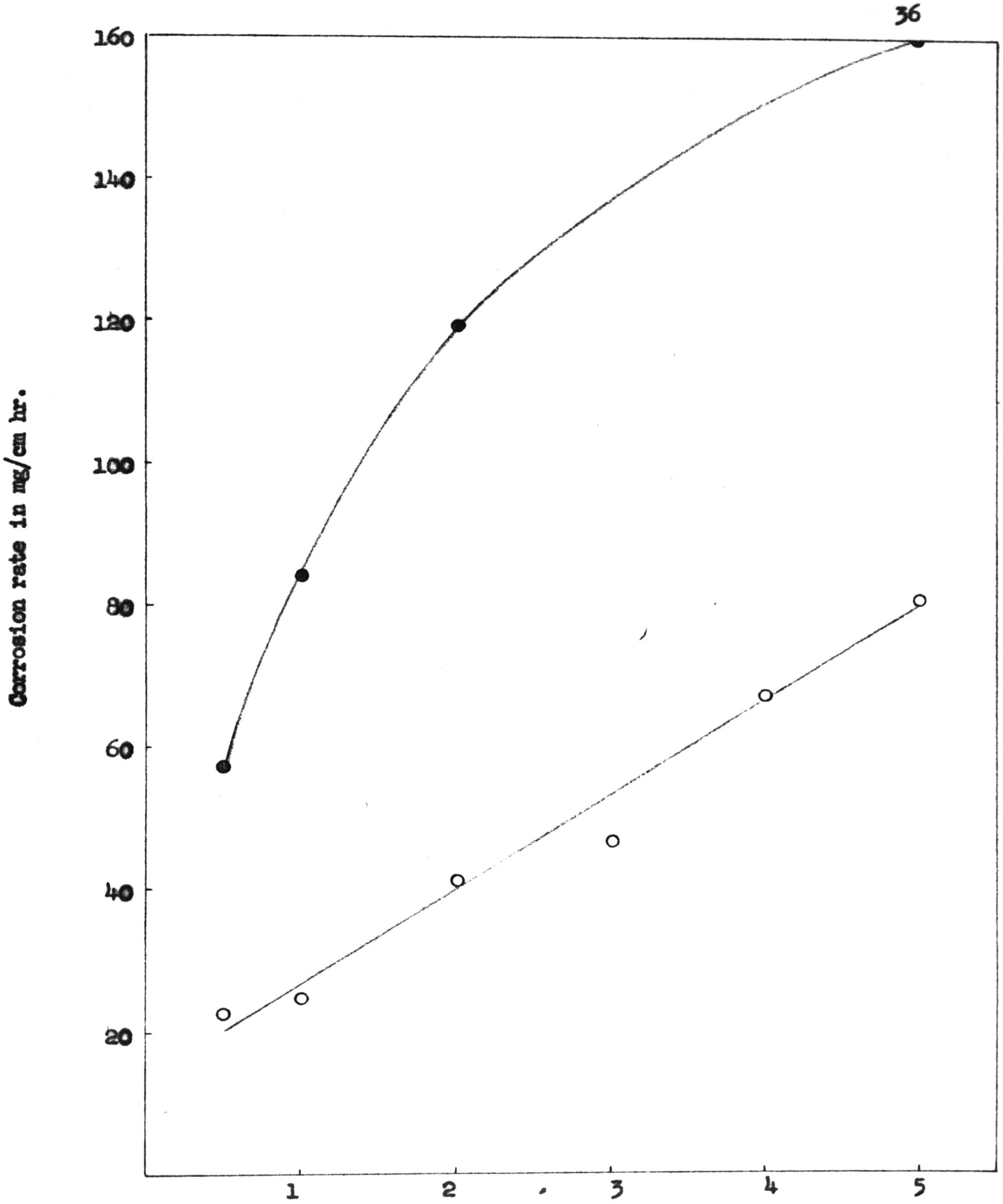


Figure 4. - Percentage of weight loss of titanium in fused NaCl containing CuCl.



Composition of $CoCl_2$ in % by weight.

● in presence of air

○ in presence of helium

Figure 5. - Corrosion rate of titanium in fused NaCl containing $CoCl_2$.

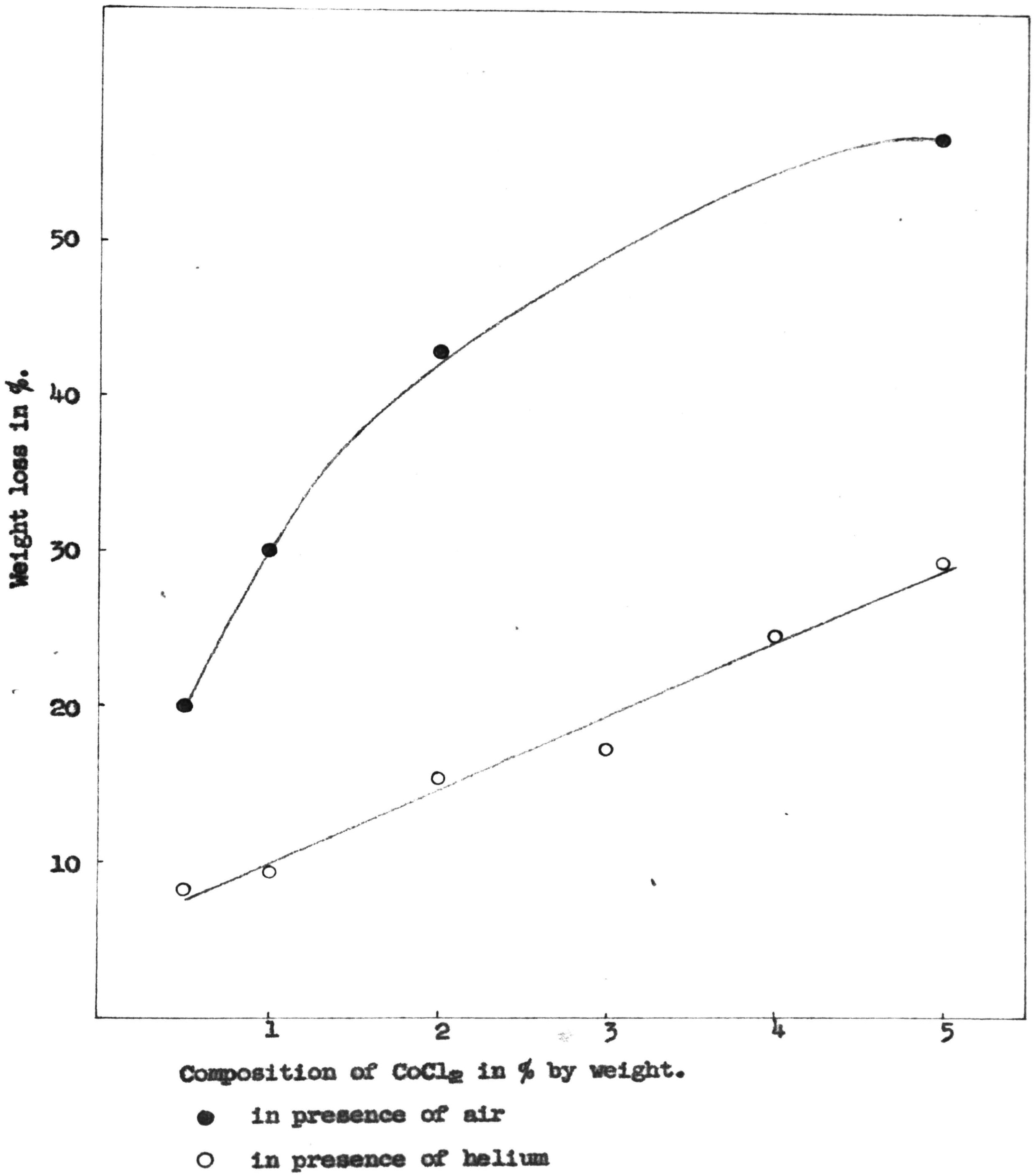
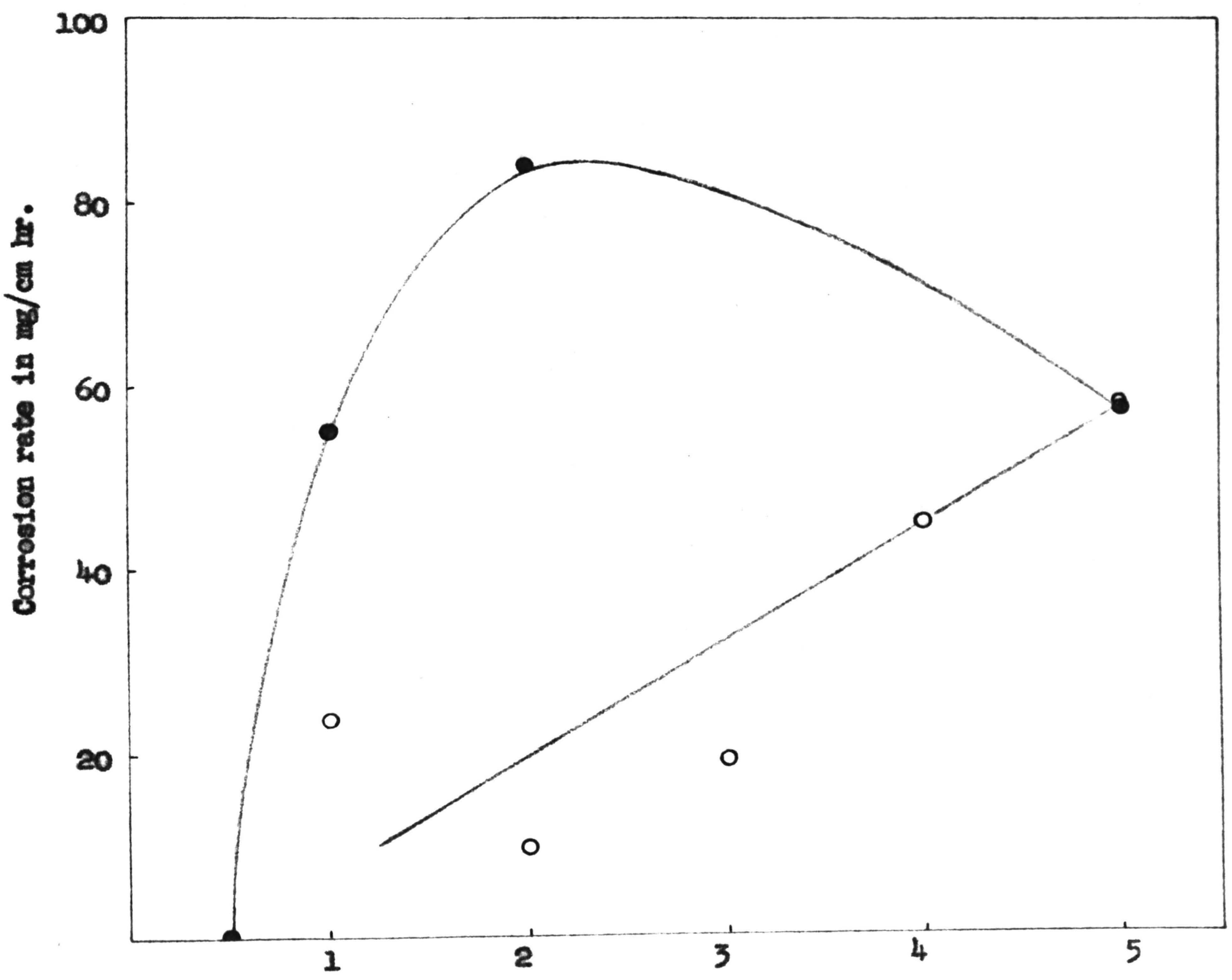


Figure 6. - Percentage of weight loss of titanium in fused NaCl containing $CoCl_2$.

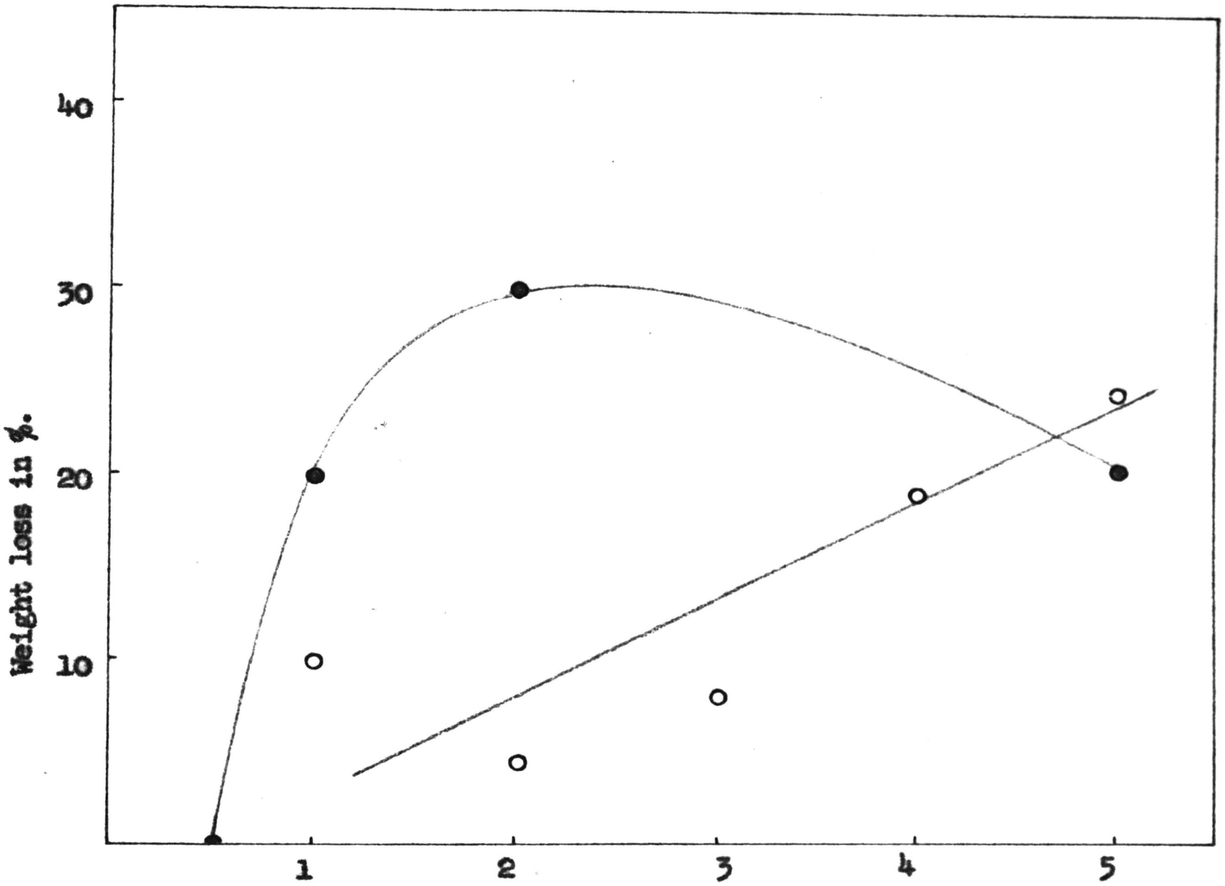


Composition of $NiCl_2$ in % by weight.

● in presence of air

○ in presence of helium

Figure 7. Corrosion rate of titanium in fused NaCl containing $NiCl_2$.



● in presence of air

○ in presence of helium

Figure 8. - Percentage of weight loss of titanium in fused NaCl containing $NiCl_2$.

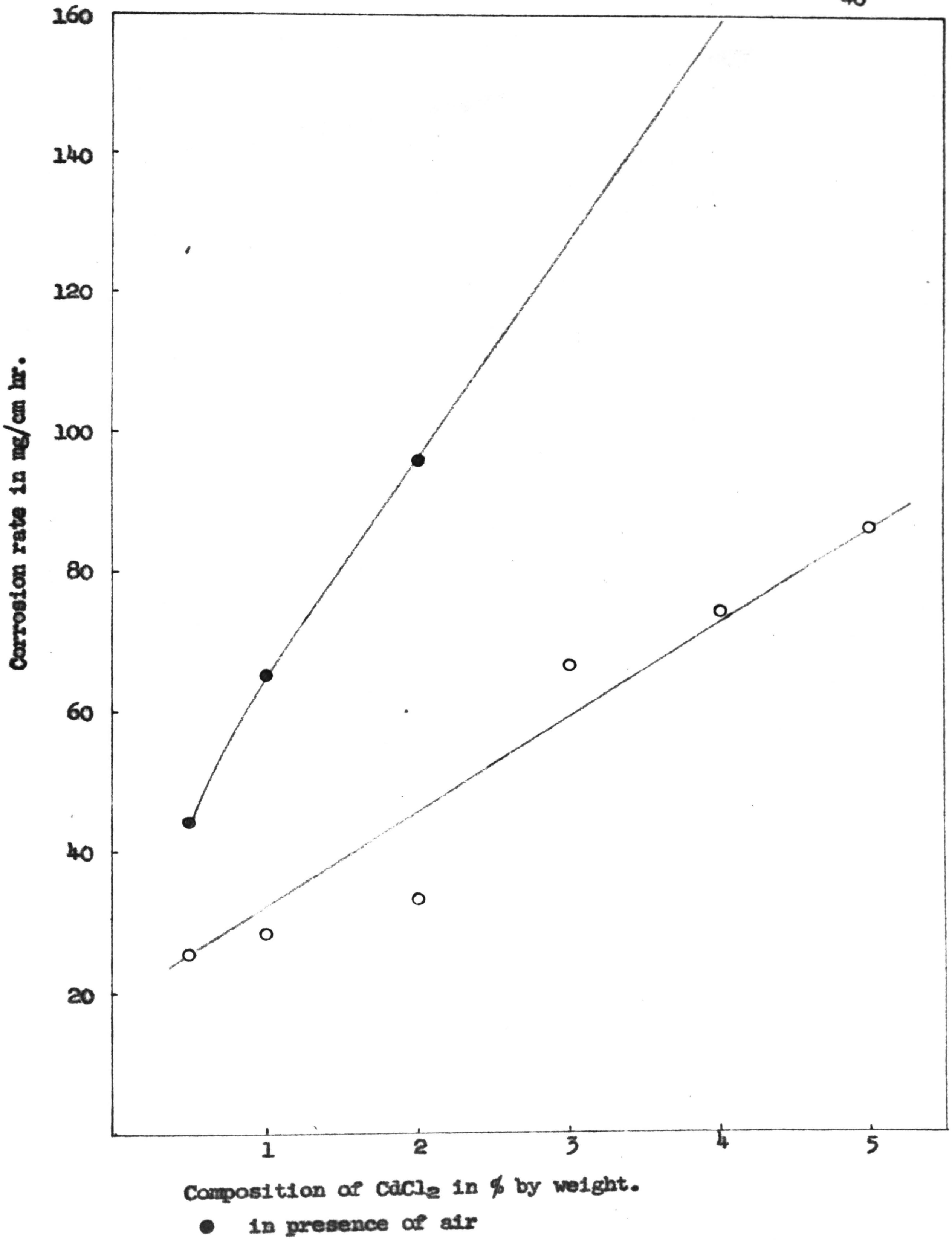


Figure 9. - Corrosion rate of titanium in fused NaCl containing CdCl$_2$.

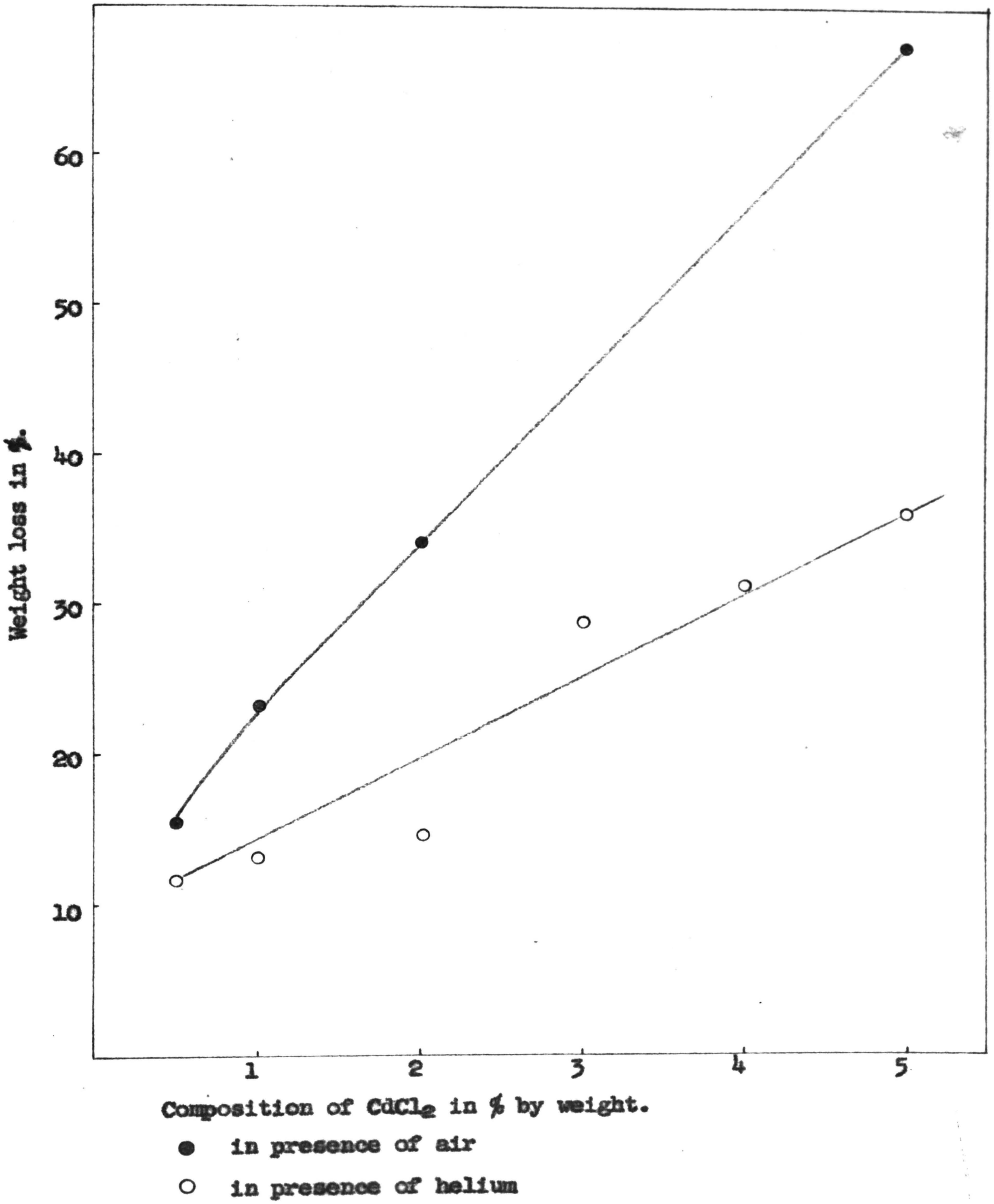


Figure 10. - Percentage of weight loss of titanium in fused NaCl containing $CdCl_2$.

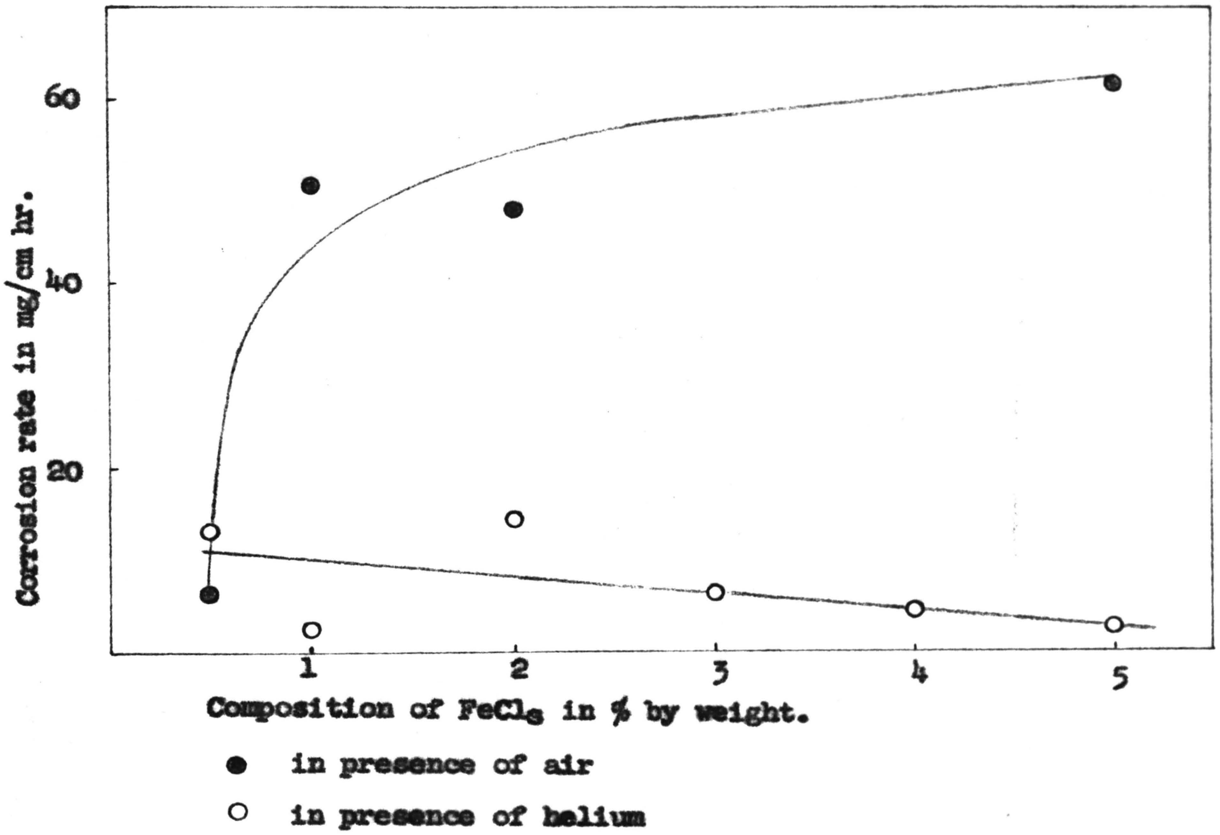


Figure 11. - Corrosion rate of titanium in fused NaCl containing FeCl$_3$.

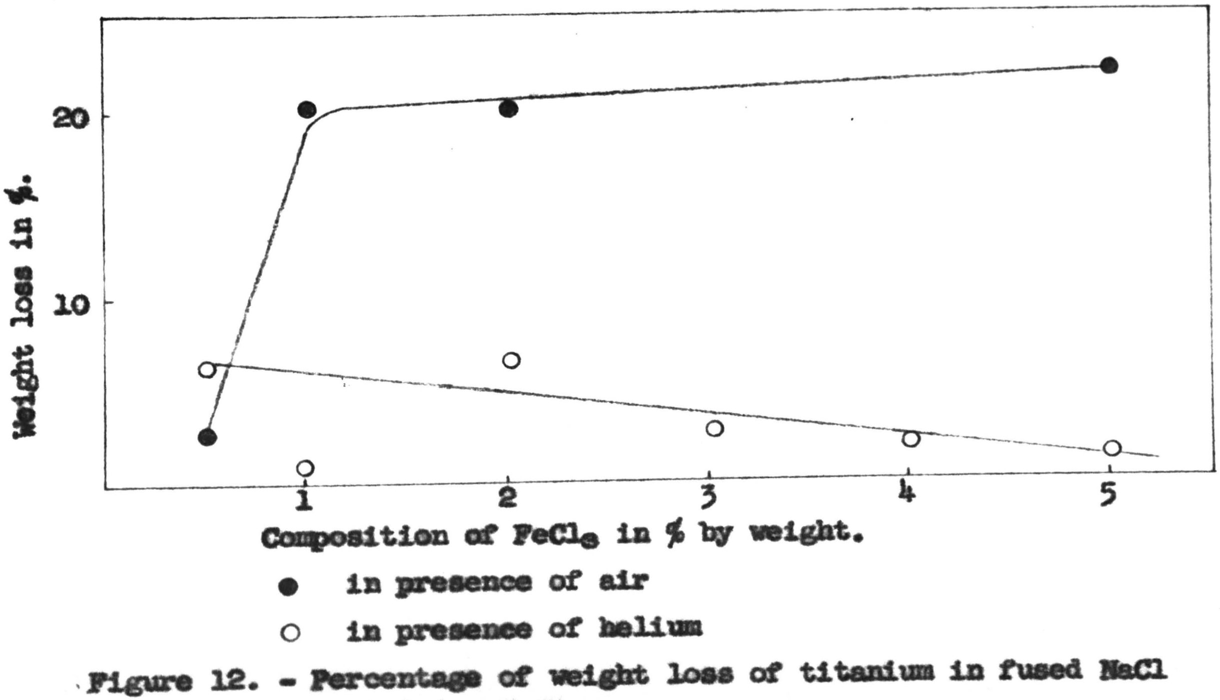


Figure 12. - Percentage of weight loss of titanium in fused NaCl containing FeCl$_3$.

Fig. 11. Fig. 4, Fig. 6, Fig. 8, Fig. 10, and Fig. 12 shows the percentages of weight loss of titanium samples due to corrosion in fused NaCl in presence of the heavy metal salts mentioned.

The corrosion rate of titanium samples under helium without any addition of heavy metal salt was found to be 0.22 mg/cm^2 hr. This figure is very small in comparison with the corrosion figures obtained under helium with heavy metal salts present.

As for the mechanism of titanium corrosion due to heavy metal salts in a fused salt bath, it is governed by the presence of air. In the last case the oxygen of the air penetrated during the experiments into the liquid salt bath and diffused to the surface of the titanium sample where it oxidized the titanium to form the titanium-oxygen solid solutions. The differential expansion of the titanium lattice and that of the oxidation products during the solid solution formation probably caused the break down of the solid solutions because of their brittleness 13). The slow corrosion of titanium which occurred under helium (without any addition of heavy metal chlorides) in liquid salt is believed to be due to the residual oxygen still present in the furnace, or due to the oxygen coming from oxides such as SiO_2 of the crucible.

To explore the corrosion process in the same liquid salt but in presence of salts of heavy metals, X-ray patterns of the corrosion products were made for identification purposes. These products were first separated into light and heavy fractions by de-

---

(13) Chiou, K. C., "Corrosion Products of Titanium in Fused Salt Baths," Master's Thesis, Missouri School of Mines and Metallurgy, 1954.

cantation, and then they were dried and ground.

In case of CuCl additions, both the heavy and light products showed only Cu lines in the X-ray patterns. The Cu lattice was expanded and the intensity of the lines decreased with increasing temperature. However, the background intensity increased under the same conditions. No titanium lines were found either in the heavy or in the light fractions. The possible reaction of the added CuCl is as follows:

$3\ CuCl + Ti \longrightarrow TiCl_3 + 3\ Cu$ (deposited on excess Ti)

so the deposited copper diffused into titanium and the latter diffused into the excess copper to form a solid solution with expansion of Cu lattice. Then the solid solution peeled off owing to the differential physical properties of the titanium and the solid solution.

X-ray patterns of the corrosion products produced in presence of $FeCl_3$ addition were also made. No distinct iron lines were present on the patterns. But there was some evidence that a solid solution of Fe in Ti was formed: weak Ti lines showed up, the position of which indicated that the original titanium lattice was expanded. The iron deposition upon titanium occurred probably according to

$FeCl_3 + Ti \longrightarrow TiCl_3 + Fe$ (deposited on excess Ti)

and the iron diffused into titanium expanding its lattice. Then the solid solution formed broke down from the titanium samples.

In case of Cd-additions to NaCl the reaction that occurred was probably similar:

$3\ CdCl_2 + 2\ Ti \longrightarrow 2\ TiCl_3 + 3\ Cd$ (deposited on excess Ti)

As the samples were made in the helium atmosphere under slight helium over pressure, it was not probable that the cadmium could evaporate from the crucible at a fast rate. As in the previous experiments no distinct Cd lines were observed on the X-ray patterns of the light and heavy products. The comparison of the films with the pure titanium pattern showed a greatly expanded titanium lattice. So the process of formation of corrosion products is the same as already described: The deposited Cd (at 850° to 900°C) formed a solid solution with Ti expanding its lattice. Then the surface alloy broke down from the sample forming a dispersion with the liquid salt. The presence of Ti in the alloy is proved by the fluorescent radiation (background darkening) produced by the Ti of the sample.

On the basis of these experiments with CuCl, $FeCl_3$, $CdCl_2$ it can be asserted that the mechanism of corrosion of titanium in presence of other salt additions is the same: alloy formation of the displaced metals with titanium on the surface of the Ti-sample and break down of the alloy layer formed. If such alloys are not formed, or the physical properties of the alloy do not differ from the Ti base metal, no dispersion with liquid salt will be formed, and there will be no corrosion. This probably happened in the case of inactive additions which are listed in Table I.

2. The effect of an additional metal on the titanium coating process.

It was shown that the titanium coating process can be improved in obtaining thicker coatings by precoating the samples with copper, silver, nickel, platinum, or gold. The average coating weights of these precoated samples were heavier than those obtained on bare iron. Co, Sn, or Cd used as precoating metals for iron did not improve the results.

Copper and silver as precoating materials were the best for obtaining thicker titanium layers. These two metals are easily deposited from their aqueous solutions upon iron and form a porous coating on it. When such samples, subsequently plated with titanium, probably formed at the high temperature of the bath, ternary alloys Fe-Cu-Ti and Fe-Ag-Ti. It is possible that the alloy formation promotes the adherence of the titanium particles coming from the dispersion simply because the melting point of the alloy was lower than that of titanium or iron.

An experiment was made to prove the presence of copper in these Cu-precoated titanium coatings. The coating was first put into 1 N HF solution to dissolve the titanium layer. The black Fe-Cu-Ti alloy appeared in flakes in the HF solution after the outer coating dissolved. The residue was separated from the HF solution by filtration, washed with distilled water, and flushed into a small test tube, where it was dissolved in 1 N HNO_3. Then an excess of NH_4OH was added to the solution and the precipitated iron hydroxide was filtered. The filtrate had a blue color indicating that in the nitric acid solutions, Cu^{++} were present, originating from the Cu of the flakes. As for Fe-Ag-Ti alloy, the amount of precoated silver present in the titanium deposit was so small that it escaped the detection. It might also be that silver diffused away or broke off before titanium was deposited upon the iron.

Nevertheless, both copper and silver are beneficial to the titanium coating process in obtaining thicker coatings. From the recoating experiments as shown in Table XIX, the following conclusion can be drawn:

Taking the weight of coatings on bare ingot iron base as unit (I), the weight of titanium coatings on Ag-precoated (II) and those on Cu-precoated samples (III) can be compared with each other. Then the ratio of (I:II:III) for the first coating turned out to be: I:II (Ag):III (Cu) = 3.896 : 4.843:5.155 = 1:1.24 : 1.132; for the second coating, I:II (Ag) : III (Cu) = 10.416 : 10.854:13.170 = 1:1.04: 1.27; for the whole, I:II (Ag) : III (Cu) = 14.312 : 15.697: 18.325 = 1:1.18 : 1.28. Both the first coating and the second coating were made at 1000°C in presence of helium. The only difference was that the former was made in one hour and the latter in three hours. That is to say, the second coating had a coating time three times as long as the first one. These figures show that the first deposit of shorter coating time had better ratios than the second deposit obtained in a longer coating time.

In addition an experiment, shown in Table XXII, was performed to acquire a very thick deposit. The values obtained were 17.895 mg/cm^2 (I) on the bare ingot iron samples, 17.373 mg/cm^2 (II) on Ag-precoated iron samples, and 23.708 mg/cm^2 (III) on Cu-precoated iron samples. The ratios are as follows:

I : II(Ag): III(Cu) = 17.895 : 17.373 : 23.708 = 1:1:1.323

Thus it seems that the predeposited silver was of no use in producing thicker Ti on the iron samples. From these arguments one might come to a conclusion that the precoated silver favours the coating process at higher temperature and shorter coating time rather than the same process for a longer coating time. Copper coatings on iron have in all cases a beneficial influence upon the titanium coating subsequently deposited.

3. Reason for the low corrosion resistance of titanium coatings.

It was found that the diffusion layer (Ti in Fe) displays a low corrosion resistance in acid solution and sea water. If there are only a few discontinuities in the titanium deposit the whole piece becomes worthless, although attacked only in a few spots. Why some places on the objects are not covered by titanium, thus producing pores in the deposit, it is not easy to explain. The titanium layer is formed by contacting of the surface of the sample with titanium-oxygen particles, dispersed in the liquid NaCl, being under the Browman motion. The particles, sticking to the surface of the object, contact each other only in a few points. In case of thin layers there will be always some uncovered spots between the particles as shown in Figure 13.

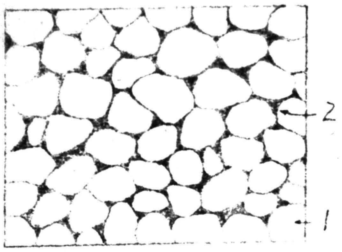


Figure 13. - Pores between particles.

1. titanium particle
2. pore

However the naked spots will be reduced in size with the continuation of the deposition process and will be further diminished by diffusion and recrystallization.

The uncovered spots were found very difficult to be sealed. If the objects were titanized with low composition of TiO_x powder, say 10% by weight TiO_x, the pores were formed by too few collisions of TiO_x particles at any instant. Since the number of collisions by the TiO_x powder is low the grain growth occurring on the surface of objects is also low, so that not many growth centers can be developed. If the coating temperature is higher and the coating time is kept longer the possibility of complete coverage of the surface seems to be improved although holes still may remain. Figure 14 shows the titanium particles forming a layer on the sample.

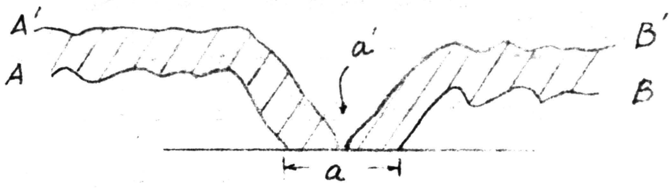


Figure 14. - Pores occurring in titanium coating.

The spot indicated by a represents a pore. Higher temperature and longer coating time will make the titanium layer thicker by growth of the particles on the surface; eventually, the level will move from AB to A'B'. There is still a place indicated by a' in the figure, which might become a pore as there might be some capillary communication with the base metal. Higher temperature and longer coating time as shown by the experiment probably cannot seal such pores, if the composition of TiO_x is normal during titanizing. Increased concentration of TiO_x, say 15% by weight is not helpful because the TiO_x particles will collide and stick to each other so that some big lumpy, porous masses will be formed on the objects.

These pores in the coatings are the places where the action of a corrosion agent can start, because as a whole, the titanium layer is completely corrosion resistant. As shown by the experiments, these pores can be partially closed by covering the titanized samples with a second coating. Such samples showed good corrosion resistance in NaCl solution, even if continued for three months. A modified, better coating process is described in the next chapter.

4. The modified titanizing process.

Based on the discussions described above and the good corrosion resistance phenomenon of the sample obtained from the recoating experiment a modified titanizing process was developed. The procedures are described on page 29 and consists of the following steps:

1. Ag-precoating of the objects
2. First Ti-coating at 1000°C
3. Slight surface scratching and washing of the objects
4. Immersing the objects in $AgNO_3$ aqueous solution
5. Second Ti-coating at 1000°C

Instead of silver, copper can be used as well; it makes thicker titanium coatings as described previously. However, it was found from experiments shown in Table XX that the Ag-precoating was superior in the pore sealing. The titanized samples were examined in 2% NaCl aqueous solution. Even the finest pores can be detected by the yellowish color of the colloidal $Fe(OH)_3$, appearing as corrosion products of iron. The pure NaCl aqueous solution for corrosion tests is better than the ferroxyl indicator (phenolphthalein + potassium ferrocyanide) which serves to detect cathodic places (where alkali is produced) as pink spots and the anodic places (where iron salts appear) as blue points. As the pores are usually very fine and the reaction is slow the color of ferroxyl solution turns dark and opaque so that the location of the pores cannot be established. In the NaCl solution all three Ag-precoated samples showed no yellow spots on the titanium layer after ten days immersion but the coatings on Cu-precoated and bare iron base showed yellow spots within 24 hours. So it was assumed that the Ag-precoated samples are better than Cu-precoated samples in obtaining a titanium layer without pores and thus the Ag-precoating was adopted in the modified titanizing process. Nevertheless by no means should the advantage of copper precoating be overlooked. It is cheap in cost and can make a thick titanium coating even on high carbon content steels.

It seems to be advantageous to produce the first coating at 1000°C (2 to 3 hours under helium) using at least 10% by weight TiO_x depending on surface condition of the sample.

After the first coating the scratched and washed samples were then immersed into an $AgNO_3$ aqueous solution. It seems to be that the silver is deposited in the opened pores and then the titanium is deposited upon this silver closing the pores in the second coating operation. The results of such a method of titanizing can be seen from Table XXI. The average total weight increase of the samples which were put into $AgNO_3$ aqueous solution twice (the second immersion came after the first coating was scratched) is 17.267 mg/cm^2 as compared with 15.561 mg/cm^2 on samples immersed in $AgNO_3$ aqueous solution only once before the first coating.

The samples which were coated by the modified process had a good corrosion resistance as already mentioned. In the final series of experiments eight of ten samples did not show any yellow spots in NaCl aqueous solution at all, as compared with none of the 44 samples titanized by the old method.

5. The future study of titanizing process.

The results of this investigation show that the titanizing process could be slightly improved by precoating the samples with copper and silver and in lesser amount by precoating with platinum, gold, and nickel. The influence of silver, as it could not be detected in the coating, is still unknown. A further investigation of the deposits might give a clue to the effect of those foreign metals. In addition there is another problem waiting for solution. It is known that medium and high carbon steels as well as cast iron were titanized only with difficulty and relatively thin and patchy titanium layers were obtained 14). The present problem seems to be

---

(14) Shih, S. T., Straumanis, M. E., and Schlechten, A. W., "Deposition of Titanium from Titanium-Oxygen Alloys on Copper, Iron, and Mild Steel," J. Electrochem. Soc., Vol. 103, p. 395, 1956.

how to seal better the pores in the titanium layer obtained on both ingot iron and high carbon steel. The effect of foreign metals in this pore sealing process might be investigated to a further detail and other better methods might be found.

This research seems to show that a sound coating cannot be obtained in one heat due to the defects in the coatings and it would be advisable to find conditions under which this would become possible. Furthermore it would be interesting to investigate the possibilities of plating of metals with metals such as zirconium, niobium, tantalum, and chromium, using the same methods as described here.

Summary

1. The rate of corrosion of titanium in fused NaCl at 900°C in presence of air was increased by small additions of $CdCl_2$, $CoCl_2$, CuCl, $NiCl_2$ and $FeCl_3$ to the NaCl.

2. Other salts shown in Table I, page 11 turned out to be inactive.

3. The rate of corrosion of titanium in fused NaCl at 900°C in presence of helium was also increased by addition of these heavy metal salts mentioned in point 1 to the NaCl.

4. The rate of corrosion of titanium in NaCl under helium in absence of these salts (see point 1) is very low.

5. The rate of corrosion increases (under helium) mostly along a straight line with the concentration of the additions (see point 1). In case of $NiCl_2$ (under air) there is a maximum at 2% $NiCl_2$. The rate (under helium) decreases with the increase of $FeCl_3$ additions.

6. The corrosion of titanium caused by these heavy metal salt additions represents a process of formation of solid solutions of the displaced metals with titanium, followed by the break down of this solid solution in small particles to form a dispersion with the liquid NaCl.

7. The coatings obtained in the titanizing process can be improved by precoating the samples with Cu and Ag and in lesser amount by precoating them with Pt, Au, Ni, in obtaining a heavier titanium coating as compared with the coatings deposited upon bare samples.

8. It was found that the titanium coating itself was completely corrosion resistant but a few pores present caused a low corrosion resistance to the titanized samples.

9. Attempts were made to seal the pores which can be done in recoating processes.

10. A modified process was developed, the essence of which is to scratch the first coating slightly and to apply a second one. Such samples usually showed a much better corrosion resistance in 2% NaCl aqueous solution than samples having only a single coating or samples having a double coating but with no intermediate slightly scratching between the application of the second coating.

BIBLIOGRAPHY

1. Gill, C. B., Schlechten, A. W., and Straumanis, M. E., "Plating Processes and Depositions," U. S. Patent No. 2,732,321, Jan. 24, 1956.

2. Gill, C. B., Straumanis, M. E., and Schlechten, A. W., "Corrosion of Titanium in Fused Chlorides," J. Electrochem. Soc., Vol. 102, p. 42, 1955.

3. Schlechten, A. W., Straumanis, M. E., and Gill, C. B., "Deposition of Titanium Coatings from Pyrosols," J. Electrochem. Soc., Vol. 102, p. 81, 1955.

4. Shih, S. T., Straumanis, M. E., and Schlechten, A. W., "Deposition of Titanium from Titanium-Oxygen Alloys on Copper, Iron and Mild Steel," J. Electrochem. Soc., Vol. 102, p. 395, 1956.

5. Chiou, K. C., "Corrosion Products of Titanium in Fused Salt Baths," Master's Thesis, Missouri School of Mines and Metallurgy, 1954.

6. Straumanis, M. E., and Chen, P. C., "The Mechanism and Rate of Dissolution of Titanium in Hydrofluoric Acid," J. Electrochem. Soc., Vol. 98, p. 234, 1951.

7. Straumanis, M. E., J. Appl. Phys., Vol. 20, p. 726, 1946.

8. Straumanis, M. E., Shih, S. T., and Schlechten, A. W., "The Mechanism of Deposition of Titanium Coatings from Fused Salt Baths," J. Electrochem. Soc., Vol. 104, p. 17, 1957.

9. Straumanis, M. E., Schlechten, A. W., "Titan-Überzuge auf Metallen und Keramischen Objekten," Metall, 10, p. 901-909, 1956.

VITA

The author was born on October 20, 1922 in Nanking, China. He received the degree of Bachelor of Science in Metallurgical Engineering in 1945 from the National Chungking University, Chungking, China. After graduation he served as a member of the engineering staff in the Anshan Iron and Steel Corporation, Anshan, China, and later as an Assistant Engineer in the Taiwan Steel Works, Formosa. In November 1955 he enrolled as a graduate student in the Metallurgical Engineering Department of the School of Mines and Metallurgy of the University of Missouri, Rolla, Missouri.