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PROGRESS REPORT  
APPLICATION OF THE POLAROGRAPH TO ANALYSIS  
OF TITANIUM-BASE ALLOYS

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SUMMARY

This report covers the period of August 7 to October 7, 1952. A "practical" or "working" bibliography of pertinent polarographic and chemical references on titanium analysis was prepared, and most of this literature has been examined. A summary of the available data on polarographic half-wave potentials for titanium and the principal titanium-alloying metals in various media has been prepared. The necessary chemical, polarographic, accessory electrical, constant-temperature, and other needed equipment has been assembled. Standard chemicals and pure materials have been located and experimental work has been started. Research on the chemical analysis of titanium-base materials in other laboratories has been investigated.

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POLAROGRAPHIC HALF-WAVE POTENTIALS FOR TITANIUM AND ITS ALLOYING CONSTITUENTS

	<u>Supporting Electrolyte</u>	<u>E<sub>1/2</sub> vs. SCE</u>	<u>Notes</u>
A. Titanium	Ti <sup>4</sup> in 0.1 N HCl	-0.81	Ti <sup>4</sup> → Ti <sup>3</sup>
	Ti <sup>4</sup> in dilute NaOH	N.R.	
	Ti <sup>3</sup> in 0.1 N HCl	-0.14	Ti <sup>3</sup> → Ti <sup>4</sup>
	Ti <sup>4</sup> and/or Ti <sup>3</sup> in acidified tartrate	-0.44	Ti <sup>4</sup> ⇌ Ti <sup>3</sup> (reversible)
	Ti <sup>4</sup> in 0.5 M H <sub>2</sub> SO <sub>4</sub>	-0.30	
B. Zirconium	0.001 M ZrOCl <sub>2</sub> in 0.1 N KCl + ca. 0.001 N HCl at pH 3	-1.65	Preceded by hydrogen wave Zr <sup>4</sup> → Zr(?)
C. Nickel	1 N KCl	-1.1	
	1 M NH <sub>4</sub> OH + 0.2 N NH <sub>4</sub> Cl	-1.02	
	1 N KCNS	-0.70	
	0.5 M pyridine + 0.5 M pyridinium chloride	-0.78	

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	<u>Supporting Electrolyte</u>	<u>E<sub>1/2</sub> vs. SCE</u>	<u>Notes</u>
	1 N KCN	-1.40	Ni <sup>2</sup> → Ni <sup>0</sup>
	1 M or greater neutral tartrate	• N.R.	
D. Manganese	Mn <sup>2</sup> in 1 N KCl	-1.51	Mn <sup>2</sup> → Mn
	Mn <sup>2</sup> in 1 M NH <sub>4</sub> OH + 1 N NH <sub>4</sub> Cl	-1.45	
	Mn <sup>2</sup> in 0.2 N KCNS	-1.55	
	Mn <sup>2</sup> in 1.5 N KCN	-1.33	With smaller conc. of CN a second wave appears at -1.8
	Mn <sup>2</sup> in 0.2 M tartrate + 2 N NaOH	-0.4 -1.7	Mn <sup>2</sup> → Mn <sup>3</sup> Mn <sup>2</sup> → Mn
	MnO <sub>4</sub> <sup>-</sup> in neutral BaCl <sub>2</sub>	(0.0)	Wave starts at zero potential
		(-1.5)	Reduction states not known
E. Aluminum	0.05 N BaCl <sub>2</sub> or KCl	-1.75	
F. Bismuth	Bi <sup>3</sup> in 0.1 N H <sub>2</sub> SO <sub>4</sub>	-0.04	Prob. Bi <sup>3</sup> → Bi
	Bi <sup>3</sup> in 0.1 N HCl	-0.08	
	Bi <sup>3</sup> in 0.1 N HNO <sub>3</sub>	-0.01	
	Bi <sup>3</sup> in 0.3 M tartrate at pH 4.5	-0.29	
	Saturated Bi(OH) <sub>3</sub> in 1 N KOH	-0.6	
G. Cobalt	Co <sup>2</sup> in 0.1 N KCl or NaCl	-1.20	
	Co <sup>2</sup> in 1 N NH <sub>4</sub> OH + 1 N NH <sub>4</sub> <sup>+</sup>	-1.30	
	Co <sup>3</sup> in 1 N NH <sub>4</sub> OH + 1 N NH <sub>4</sub> <sup>+</sup>	-0.3 -1.3	Co <sup>3</sup> → Co <sup>2</sup> Co <sup>2</sup> → Co
	Co <sup>2</sup> in 0.1 M pyridine + 0.1 pyridinium chloride	-1.07	
	Co <sup>2</sup> in 1 N KCNS	-1.03	
	Co <sup>3</sup> in 1 N KCN	-1.25	Co <sup>3</sup> → Co <sup>2</sup>
	Co <sup>2</sup> in 1 M tartrate sol'n	-1.6	
H. Iron	Fe <sup>3</sup> in HCl, HCl, HClO <sub>4</sub> , etc.		Diffusion current of Fe <sup>3</sup> → Fe <sup>2</sup> obtained at zero applied emf.

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	<u>Supporting Electrolyte</u>	<u>E<sub>1/2</sub> vs. SCE</u>	<u>Notes</u>
	Fe <sup>2+</sup> in 0.1 N KCl or BaCl <sub>2</sub>	-1.3	Fe <sup>2+</sup> → Fe
	Fe <sup>2+</sup> in 1 N NH <sub>4</sub> ClO <sub>4</sub>	-1.45	
	Fe <sup>3+</sup> and/or Fe <sup>2+</sup> in 1 M potassium oxalate	-0.24	Fe <sup>3+</sup> ⇌ Fe <sup>2+</sup> (reversible)
	Fe <sup>3+</sup> in 1 N KF	-1.36	Fe <sup>3+</sup> → Fe <sup>2+</sup>
	Fe <sup>3+</sup> in 0.5 M sodium citrate	-0.35	Fe <sup>3+</sup> → Fe <sup>2+</sup>
	Fe <sup>3+</sup> and/or Fe <sup>2+</sup> in alkaline tartrate solution	-0.9	Fe <sup>3+</sup> ⇌ Fe <sup>2+</sup> (reversible)
	Fe <sup>3+</sup> in 1 M (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	-0.44	Fe <sup>3+</sup> → Fe <sup>2+</sup>
	Fe <sup>3+</sup> in 1 N KOH + 8% mannitol	-1.52	Fe <sup>2+</sup> → Fe <sub>2</sub>
		-0.9	Fe <sup>3+</sup> → Fe
		-1.5	Fe <sup>2+</sup> → Fe
	Saturated Fe(OH) <sub>2</sub> in 1 N NaOH	-1.46	Fe <sup>2+</sup> → Fe <sup>-4</sup>
	Fe(CN) <sub>6</sub> <sup>3-</sup> in 0.1 N KCl	(+0.2)	Fe(CN) <sub>6</sub> <sup>3-</sup> → Fe(CN) <sub>6</sub> <sup>4-</sup>
I. Chromium	Cr <sup>3+</sup> in 0.1 N KCl or NH <sub>4</sub> ClO <sub>4</sub>	-0.88	Cr <sup>3+</sup> → Cr <sup>2+</sup>
		-1.53	
	Cr <sup>3+</sup> in sat. tartaric acid	-1.00	Prob. Cr <sup>3+</sup> → Cr <sup>2+</sup>
	Cr <sup>3+</sup> in 0.1 M pyridine + 0.1 N pyridinium chloride	-0.95	
	CrO <sub>4</sub> <sup>2-</sup> in 1. N NaOH	-0.85	Cr <sup>6+</sup> → Cr <sup>3+</sup>
	CrO <sub>4</sub> <sup>2-</sup> in 0.1 N KCl	-0.3	
		-1.0	Cr <sup>6+</sup> → Cr <sup>3+</sup>
		-1.5	Cr <sup>3+</sup> → Cr <sup>2+</sup>
		-1.7	Cr <sup>2+</sup> → Cr
	CrO <sub>4</sub> <sup>2-</sup> in 0.1 N NH <sub>4</sub> Cl + NH <sub>4</sub> OH at pH 8 to 9	-0.35	Cr <sup>6+</sup> → Cr <sup>3+</sup>
		-1.7	Cr <sup>3+</sup> → Cr
J. Tungsten	W <sup>6+</sup> in neutral or alkaline medium	N.R.	
	W <sup>6+</sup> in 10 N HCl	-0.42	reduction state not known
K. Vanadium	V <sup>3+</sup> in 0.01 N HCl + 0.1 N KCl	-0.85	V <sup>3+</sup> → V <sup>2+</sup> (?)
	V <sup>5+</sup> (NH <sub>4</sub> VO <sub>3</sub> ) in 0.1 N HCl	(0.0)	V <sup>5+</sup> → V <sup>4+</sup>
		-0.8	V <sup>4+</sup> → V <sup>2+</sup>
	VO <sub>3</sub> <sup>-</sup> in 0.1 N LiOH	(-1.7)	
	VO <sub>3</sub> <sup>-</sup> in 6 N NH <sub>4</sub> OH + 0.2 N NH <sub>4</sub> Cl	-1.6	V <sup>5+</sup> → V <sup>2+</sup> (?)

SUMMARY OF RESULTSA. Assembly of Apparatus

While automatic-recording instrumentation may be desirable at a later stage of the investigation, a manual-type Fisher polarograph (Electropode) has been calibrated (galvanometer shunts and potential scale) for the exploratory runs. The "H"-style cell with a saturated calomel reference electrode and water jacketing on the solution side will be employed. A constant-temperature bath using a circulating pump, a fixed-setting thermostat, and a Fisher-Serfass electronic relay is being employed for the temperature control. Temperature, at present, will be maintained at  $25 \pm 0.1^\circ\text{C}$ ; but the fixed-temperature regulator is easily exchangeable for work at other temperatures.

B. Preliminary Study of Titanium Solutions

Standard samples of titanium dioxide and titanium alloys were obtained from the National Bureau of Standards. A 5 mM stock solution of titanium was prepared from the standard  $\text{TiO}_2$ . A trial polarogram was run on an aliquot portion of the stock solution in a 0.1 M sodium fluoride medium as supporting electrolyte. The polarogram shows a well-defined wave at approximately -0.14 volts vs. SCE.

The dissolution of  $\text{TiO}_2$  materials proceeds with some difficulty, and the choice of solvents is limited. This is undesirable for our purposes, since it predetermines and limits the number of polarographic supporting media which could be examined. A small specimen of Foote Mineral Co. 99.99% titanium metal bar has been obtained (and more is on order) to furnish the titanium background for testing the polarography of alloying metals in a variety of media.

C. Current Status of Titanium Analysis

At the present time a variety of agencies are interested in the determination of the minor constituents in titanium metal and in titanium-base alloys. Although it was believed that only slight use was being made of polarographic technique, it seemed important to ascertain the present knowledge on the chemical analysis of titanium materials. Accordingly, during August and September an attempt was made to learn by extensive correspondence the present status of work on the analysis of titanium-base



alloys and titanium metal which is being sponsored by the Navy and Army Departments of the Department of Defense. Letters were exchanged with Watertown Arsenal, which is sponsoring and coordinating research on methods of analysis of titanium and its alloys. In addition, letters and one personal visit were exchanged with six industrial and arsenal laboratories working on the general problem. Watertown Arsenal has fully approved cooperation with us on the part of its contractors. As a result, we have received copies of a considerable number of analytical procedures for the photometric, gravimetric, and titrimetric determination of minor constituents in titanium-base materials, which will be of considerable help to us in the preparation of solutions for polarographic investigation.

#### FUTURE WORK

We propose to examine the following possibilities in the order named, within the period of the next two to four months.

(1) The polarography of titanous solutions in a variety of supporting electrolytes in order to ascertain how many of the alloying metals would be determinable at more positive potentials than the titanous/titanous reduction-wave in each medium.

(2) Conditions for the quantitative reduction of titanium to the  $Ti^{3+}$  stage in various media, and the relative difficulties of maintaining the reduced state in each case.

(3) The polarography of titanous solutions in various media and the separation of the waves of alloying metals from the ous/ic oxidation and from the ous/metal reduction.

We shall try to correspond and cooperate in every way possible with all other projects concerned with analysis of titanium.

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