

ELECTRODEPOSITION OF TITANIUM

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FOREWORD

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WADC TR 54-485 Pt 2

Contrails

ABSTRACT

The study of titanium-aluminum alloy baths as described in WADC TR 54-485 Part 1 was continued.

The preparation of concentrated titanium-aluminum and zirconium-aluminum alloy baths by other means than use of the difficultly obtainable borohydrides of titanium and zirconium was investigated. This was done by reacting in an ether solution boron trichloride, lithium aluminum hydride, aluminum chloride, and titanium or zirconium tetrachloride. Under the experimental conditions used this method was not successful.

An investigation was made of the possibility of using alcohols as complexing agents in solutions of titanium halides. No metallic deposits were obtained from this type of bath.

The unavailability of lithium borohydride (used to prepare titanium and zirconium borohydrides) from commercial sources made necessary an examination of methods for preparing this compound and a quantity was prepared.

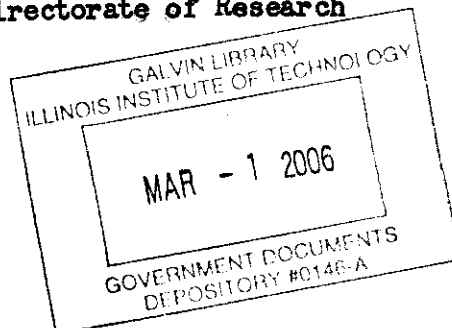
PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



R. W. CONNORS
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WADC TR 54-485 Pt 2

iii

Contrails

Contrails

Introduction

The electrodeposition of titanium from organic solvents has been shown in this laboratory to be most promising in ether type solvents containing as solutes titanium compounds such as titanium borohydride.

A mixed type of bath containing titanium borohydride, lithium aluminum hydride, and aluminum chloride has yielded titanium-aluminum alloy deposits containing up to 6.5% titanium. Similarly when zirconium borohydride was used instead of titanium borohydride in these baths, zirconium-aluminum alloy deposits were obtained containing up to 45% zirconium. The preparation of these baths is described in WADC TR 54-485 Part 1.

Ether Solutions of Titanium Borohydride

For further investigation of the borohydride alloy baths it was necessary to prepare more titanium and zirconium borohydride. Since the methods we have been using were time consuming and involved handling the pure borohydrides, which ignite spontaneously on exposure to the atmosphere, a more efficient and safer method of preparing these baths was sought.

The borohydride aluminum-hydride baths were prepared in three different ways: (1) boron trifluoride etherate was added to an ether solution of lithium aluminum hydride followed by the addition of titanium or zirconium tetrachloride, (2) use of boron trichloride etherate in place of boron trifluoride etherate as above, and (3) passage of gaseous boron trichloride into an ether solution of lithium aluminum hydride followed by the addition of titanium or zirconium tetrachloride to the resulting solution. The use of boron trifluoride proved to be unsatisfactory as insoluble fluorides such as lithium fluoride and aluminum fluoride were formed. The large amount of

WADC TR 54-485 Pt 2 1

Conclusions

solids formed in these baths resulted in a sludge which made electrolysis inconvenient. No satisfactory deposit was obtained from any of the titanium baths studied, however alloy deposits containing zirconium and aluminum were obtained from the similarly prepared zirconium baths.

An intermediate in the formation of these baths was diborane. Under the experimental conditions used it was found that the extent of reaction of this compound with lithium aluminum hydride to form aluminum borohydride was very low and that most of the diborane escaped from the reaction vessel. This low yield of aluminum borohydride would partially explain the inability to obtain a satisfactory titanium bath.

The baths described above are listed in Table I. Number six was found to be the most satisfactory.

The reaction of alkali metal borohydrides such as lithium borohydride with various titanium halides in ether solutions offers a convenient means of preparing titanium borohydride solution for use as plating baths. For this reason a series of experiments was performed in which various titanium halides were reacted with lithium borohydride in ether solution. These are summarized in Table II. In all cases the formation of a color or the ability of the solution to give an alloy deposit was taken as evidence of reaction. Each solution was electrolyzed at various current densities, alone and with aluminum hydride plating bath added. All of the titanium halides used reacted with lithium borohydride regardless of the ratio of titanium halide to lithium borohydride. The relative reactivities of the halides were iodide > bromide > chloride. The tetravalent compounds were more reactive than the trivalent. From the colors formed in ether solutions it appears that the tetravalent bromide and to a lesser extent the iodide react like the chloride to form a halo-borohydride of the type $Ti(BH_4)_2X$. None of these mixed halide

Contrails

borohydride compounds of titanium in ethyl ether gave a metallic deposit when electrolyzed directly even though most of them did conduct well. All of these solutions gave an alloy deposit containing aluminum when aluminum hydride plating bath was added.

The possibility of electrodepositing titanium from a concentrated ether solution of a mixed halo-borohydride of titanium was investigated. Lithium borohydride was reacted with titanium halides using the mole ratio 0.25. The halides used were: titanium tetrabromide, titanium tetraiodide, titanium tribromide, and titanium tetrachloride. The concentration of titanium borohydride formed was about 1.6M in each case. Each solution yielded only a black, moisture-sensitive deposit when electrolyzed. In these baths phenyl acetylene and tetrahydrofuran were used as possible complexing agents but they were found to be without effect.

The effect of using aluminum hydride (AlH_3) instead of lithium aluminum hydride ($LiAlH_4$) in the titanium-aluminum alloy bath previously described was investigated. It was found that the stability of the baths was increased slightly but the titanium content of the titanium-aluminum alloys remained about the same, i. e., 6.5 percent.

The Preparation of Lithium Borohydride

Lithium borohydride, which is used as an intermediate in preparing titanium and zirconium borohydrides, has become increasingly difficult to obtain commercially and is now available only as a special order at a price of about \$2.00 per gram.

For this reason we investigated the preparation of this compound by various methods involving the much cheaper potassium borohydride. The fusion of potassium borohydride with lithium chloride or lithium chloride-potassium chloride eutectic mixture

Contrails

yielded a solid from which a small amount of lithium borohydride could be extracted with ethyl ether. Since this method was unsatisfactory we have prepared this compound by the method of Paul and Joseph (Bull. Soc. Chim. p. 758, 1953). In this procedure lithium borohydride is formed from the reaction of lithium chloride with potassium or sodium borohydride in tetrahydrofuran.

Preliminary studies have shown that it may be possible to avoid the use of lithium borohydride by preparing titanium or zirconium borohydrides directly in ether solution from the reaction of potassium borohydride with titanium or zirconium tetrachloride.

Alcoholic Solutions of Titanium Halides

Various alcoholic solutions of titanium halides were investigated as plating solutions. These are listed in Table III. The alcohols contained 10 percent by weight of each of the above titanium halides and were saturated with hydrogen chloride before electrolysis. Many of the solutions listed in the table underwent a color change when hydrogen chloride was added which was taken to indicate the formation of a complex. Electrolysis of these solutions did not yield a deposit.

This series of experiments was repeated with an excess of titanium tetrachloride added to each solution. Electrolysis of these solutions yielded a deposit only in the case of titanium trichloride in 2-propynol. This was a black non-metallic deposit.

Silicone Compounds

A literature survey was begun of silicone compounds for use as solvents, complexing agents, and possible intermediates in the preparation of new titanium compounds.

Contrails

A quantity of these compounds is now on hand for evaluation in titanium baths.

WADC TR 54-485 Pt 2 5

Table I

Deposition of Titanium and Zirconium-Aluminum Alloys from Hydride-Borohydride Type Baths Prepared from Boron Trichloride and Lithium Aluminum Hydride

	<u>Reactants</u> (moles/l)				<u>Remarks</u> (c.d. = 0.4 amp/dm ² throughout)
	<u>LiAlH₄</u>	<u>BCl₃</u>	<u>ZrCl₄</u>	<u>TiCl₄</u>	
1.	0.6	0.6	0.15	-	{Black deposit. LiAlH ₄ added to bath gave grey to silvery deposit.
2.	0.6	0.6	0.3	-	Same as 1.
3.	1.2	0.6	0.15	-	{Solution solidified on adding ZrCl ₄ . Ether extract gave fair deposit containing Zr.
4.	0.8	0.6	0.3	-	No deposit until LiAlH ₄ added.
5.	0.9	0.6	-	0.18	{Bath decomposed on addition of TiCl ₄ . No deposit obtained.
6.	0.9	0.6	0.15	-	Good deposit.

Table II

Electrolysis of Ethereal Titanium
Borohydride Solutions

	<u>Titanium Halide</u>	<u>Ti/LiBH₄</u> (Moles)	<u>Color of Solution</u>	<u>Conductivity</u>	<u>Deposit Obtained When Aluminum Hydride Plating Bath Added</u>
1.	TiBr ₃	0.25	green	good	silvery
2.	"	0.33	"	"	"
3.	"	0.5	brown	"	grey-black
4.	"	1.0	"	fair	grey-silvery
5.	TiBr ₄	0.25	blue	good	silvery
6.	"	0.33	red	"	grey-black
7.	"	0.50	brown	fair	silvery
8.	"	1.0	red	poor	"
9.	TiI ₄	0.25	green-blue	good	"
10.	"	0.33	green	"	grey
11.	"	0.50	red	"	"
12.	"	1.0	red-brown	"	"
13.	TiCl ₄	0.25	black	good	---

Note: The concentration of titanium halide was 0.3 moles/l in all cases. With the exception of bath No. 8, which gave no deposit at all, a black moisture sensitive deposit was obtained in all cases when the borohydride solutions were electrolyzed. The addition of aluminum hydride plating bath to these solutions gave metallic deposits of varying quality as shown in the last column.

Contrails
Table III

Electrolysis of Alcoholic Solutions
of Titanium Halides

<u>Solvent</u>	<u>Halide</u>	<u>Conductivity</u>	<u>Nature of Deposit</u>
Ethanol	TiBr ₃	good	none
"	TiCl ₃	"	"
2-propynol	TiCl ₃ , Ti(OC ₃ H ₇) ₄	"	"
"	TiBr ₃ , NaTiCl ₄	"	"
Propylene glycol	TiBr ₃	"	"
"	TiCl ₃	"	"
Methanol	TiCl ₃	"	"
"	TiBr ₃	"	"
3,6-dimethyl-4-octyne-3,6-diol	"	poor	"
"	TiCl ₃	"	"
3-methyl-1-pentyn-3-ol	TiCl ₃ , Ti(OC ₃ H ₇) ₄	"	"
"	NaTiCl ₄	"	"
"	TiBr ₃	"	black
2-methyl 3-butyn-2-ol	TiCl ₃ , Ti(OC ₃ H ₇) ₄	"	none
"	NaTiCl ₄	fair	"
"	TiBr ₃	good	black
2,5-dimethyl 3-hexyn-2,5 diol	TiCl ₃	poor	--
"	TiBr ₃	"	none
1,3-butylene glycol	TiBr ₃	--	--
"	TiCl ₃	good	none
2,3-butylene glycol	TiCl ₃	poor	"
"	TiBr ₃	"	"

Note: In those cases where the alcohols used were solids diethyl ether solutions were used.