



DEPARTMENT OF
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*THE BROMINATION OF TITANIUM,
THORIUM, AND TITANIUM-THORIUM
AND TITANIUM-THORIA ALLOYS*

L. G. RIPLEY

MINERAL SCIENCES DIVISION

JUNE 1970

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Information Canada
Ottawa, 1970

Mines Branch Research Report R218

THE BROMINATION OF TITANIUM, THORIUM, AND
TITANIUM-THORIUM AND TITANIUM-THORIA ALLOYS

by

L. G. Ripley*

ABSTRACT

The development and appraisal of a method of bromination of titanium, thorium, and titanium-thorium and titanium-thoria alloys at temperatures of 200 to 500°C are described.

The results obtained give a clearer understanding of the reactions occurring in these types of material when they are prepared from the melt. It is concluded that titanium does not reduce thoria during the melting of a titanium-thoria alloy.

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Direction des mines

Rapport de recherches R 218

LA BROMURATION DU TITANE, DU THORIUM ET DES ALLIAGES
TITANE-THORIUM ET TITANE-THORINE

par

L. G. Ripley*

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RÉSUMÉ

Le présent rapport décrit la mise au point et l'évaluation d'une méthode de bromuration du titane et du thorium ainsi que des alliages titane-thorium et titane-thorine à des températures de 200°C à 500°C.

Les résultats obtenus font mieux comprendre les réactions que subissent ces matériaux lorsqu'ils sont préparés à partir de la fonte. On peut conclure que le titane ne réduit pas la thorine durant la fusion d'un alliage titane-thorine.

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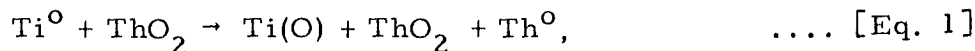
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INTRODUCTION

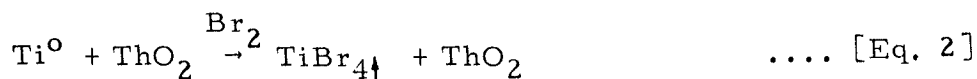
A method of producing dispersion-hardened titanium alloys by the addition of cerium or lanthanum has been described by Nicholas J. Grant (1). In the same paper, a method for determining the quantity of cerium that had been oxidized was also detailed. This procedure involved a bromination at 200°C. At this temperature, titanium and bromine react to form TiBr_4 , which can be flushed from the system with helium. The residue contains all the unreacted compounds as well as any non-volatile bromides. The oxygen dissolved in the titanium (indicated hereafter as Ti(O)) is not removed but stays with the residual titanium; this latter will be removed as TiBr_4 only when there is titanium in excess of the amount necessary to form TiO_2 with the available oxygen. Any free cerium metal would form CeBr_3 , which should also remain in the residue.

Recently, in the Physical Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Mr. C. F. Dixon and Dr. H. M. Skelly have been using thorium, instead of cerium or lanthanum, for the same purpose. Since it has become desirable to know more about the over-all reaction, a request was made to the Mineral Sciences Division of the Mines Branch to perform some bromination experiments on several samples. From these analyses it was hoped to determine whether the reaction shown in Eq. 1, below, occurred during the preparation of the alloy:

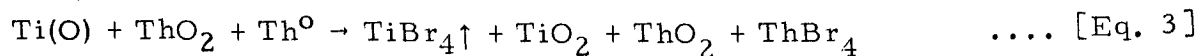


where Ti^0 and Th^0 indicate the elements in the metallic state. In other words, has the titanium reduced some of the thoria to form metallic thorium and a solid solution of oxygen in titanium $[\text{Ti(O)}]$?

The products of bromination of the materials quoted in Eq. 1 differ from one side of the equation to the other. If only Ti^0 and ThO_2 , i.e. the reactants, were present, the bromination products would be:



The TiBr_4 would be volatilized, whereas ThO_2 , which is not attacked by bromine, would be in the residue. However, the bromination of the right-hand side of Eq. 1 should proceed as follows:



Thus the titanium-oxygen solid solution would brominate to give:



The TiBr_4 is volatilized whereas TiO_2 , which is not attacked by bromine, would be in the residue. In Eq. 3 it is assumed that ThBr_4 is not volatilized at the temperatures employed, since it does not sublime rapidly until a temperature of 610°C is reached. Therefore, two approaches to the analysis are possible. Firstly, the presence of ThBr_4 , which could be established by either physical or chemical means, would indicate that Eq. 1 had occurred, whereas the second approach would be to determine the difference between the titanium concentration in the residues from brominated alloys containing ThO_2 and that in those which did not. Hence, if more titanium were found in the alloy residues, then the reaction shown in Eq. 1 has occurred.

EXPERIMENTAL

A. Apparatus

An all-Pyrex combustion system was designed and assembled; it is shown in Figure 1. (Grant's paper (1) did not describe his apparatus; therefore, the experimental conditions in the present work may be quite different from those existing in his experiments.)

This apparatus was designed to permit pre-sweeping with high-purity helium to remove all atmospheric oxygen, prior to the addition of bromine. Calcium chloride was placed in the lower flask to remove

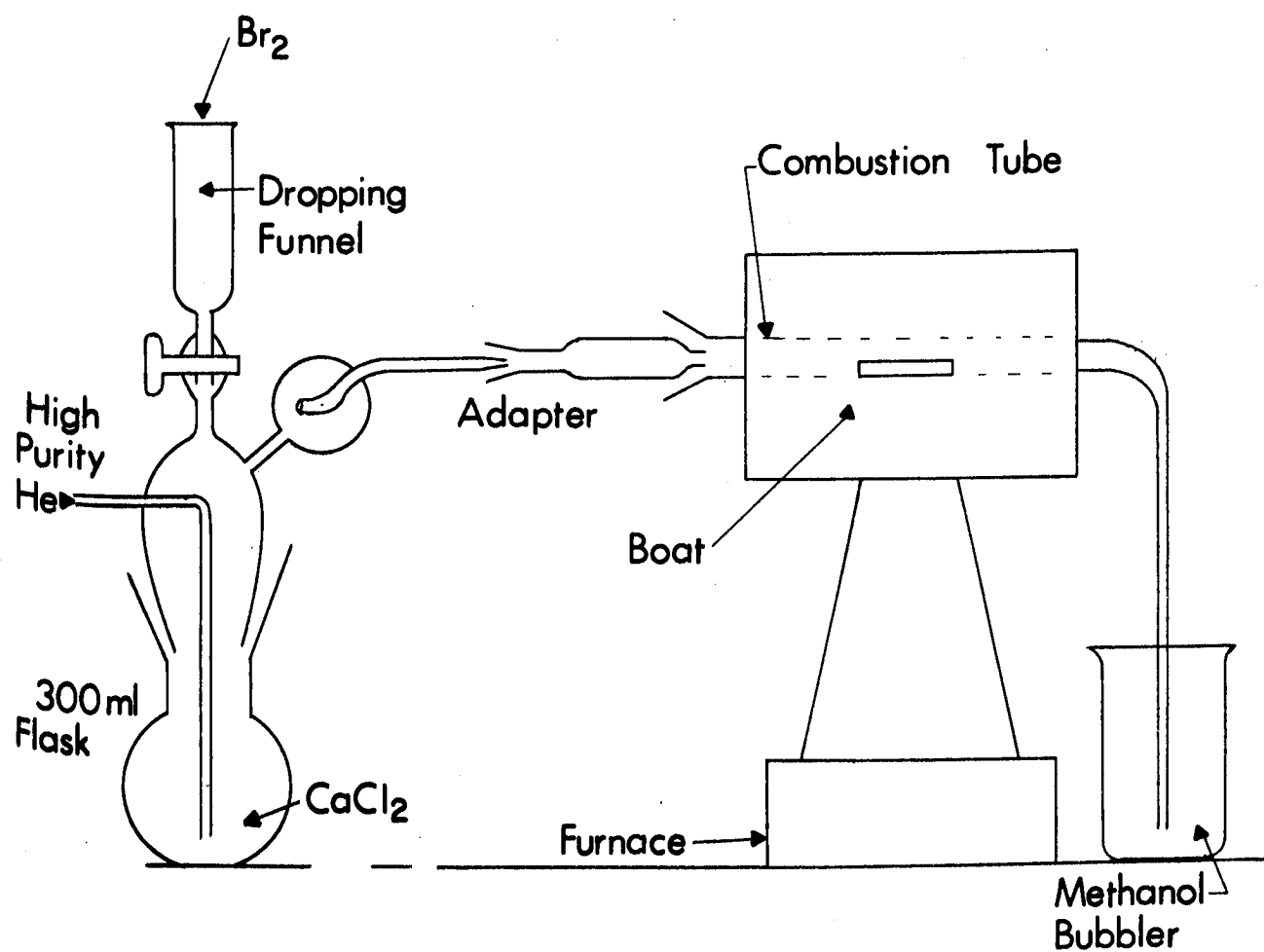


Figure 1. Bromination apparatus.

moisture from the bromine. Vitreosil boats capable of holding one gram of sample turnings were used. The excess bromine was trapped in a methanol bubbler.

B. Samples Examined

Four samples were submitted:

- a) Titanium, No. 2557, in two forms, viz., massive and turnings;
- b) Thorium, in lump form;
- c) Titanium + 2.2% thorium, Lab. No. 467, coded as A-VJ and in the form of turnings;
- d) Titanium + 2.5% thoria, Lab. No. 2556, coded as A-VC for massive material and as A-VK for turnings.

C. Preparation of Samples

Some of the experiments were performed on the material as received. In others, attempts were made at removing the surface oxide film from massive specimens, as well as from turnings, using an etchant containing 10 ml H_2O , 10 ml HNO_3 and 2 ml HF ; these attempts, however, were not successful. The etchant dissolved the surface of the specimen but, on subsequent drying, the surface became re-contaminated with a fresh oxide film.

Oily films resulting from milling the alloys were successfully removed with either methanol or isopropyl ether.

D. Bromination Procedure

A prepared sample was weighed in a Vitreosil boat and placed into the combustion system at room temperature. Atmospheric oxygen was removed by flushing with high-purity helium. Bromine was added through the dropping funnel into the flask. The helium gas carried the bromine vapour into the combustion tube, and the excess was trapped in methanol. The quantity of bromine used was a ten-fold excess over that

required by the stoichiometry. The furnace temperature was raised from room temperature to the desired level and held constant while all the bromine was being carried to the combustion zone, and continued for an additional period of after-sweeping to ensure that all the bromine vapour and volatile products had been removed from the residue. After cooling, the boat containing the residue was weighed and its percentage calculated.

The composition of the residue was determined by physical and chemical analyses; the former were by X-ray diffraction and by X-ray fluorescence. The chemical analyses were based on a methanol leaching of the residues to remove bromides and to leave the oxides unattached. The methanol-soluble portion was analysed for thorium by a gravimetric precipitation using sodium hydroxide, and for bromine by a gravimetric silver-bromide precipitation.

The reliability of these techniques of chemical analysis was demonstrated by using two synthetic mixtures of KBr and $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$. The results are shown in Table 1. Titanium would have behaved similarly to thorium in this method and, if present in the system, would have been isolated with the thorium.

TABLE 1

Chemical Analysis of Synthetic $(\text{KBr} + \text{Th}(\text{NO}_3)_4 \cdot \text{H}_2\text{O})$ Solutions

	Bromine		Thorium	
	Added	Found	Added	Found
Sample I	0.0138 g	0.0139 g	0.0111 g	0.0116 g
Sample II	0.0167 g	0.0169 g	0.0057 g	0.0059 g

E. Results and Discussion

The results of the brominations of the four submitted samples, viz., titanium thorium, (titanium + 2.2% thorium) alloy, and (titanium + 2.5% thoria) alloy, are recorded in separate tables and, since not all the residues were analysed, it is more convenient to record these analyses in the respective tables, beginning with Table 2 for titanium.

TABLE 2
Bromination of Titanium

Form of Sample	Surface Treatment	Bromination Temperature (°C)	% Residue(c)
Massive	Etchant	400	28.90
		380	11.67(a)
Massive	Etchant	500	22.85
Massive	Etchant	540	12.15
Turnings	None	200	100.00
Turnings	None	290	47.62
Turnings	None	500	1.58(b)
Turnings	None	380	0.48
Turnings	None	400	0.53
Turnings	Etchant	390	0.43

- NOTES: (a) Second bromination.
(b) X-ray diffraction analysis indicates the presence of rutile (TiO₂).
(c) No chemical analysis was performed on these residues.

It is evident from Table 2 that massive samples are brominated extremely slowly at temperatures up to 500°C, and that a temperature of approximately 380°C is required for the turnings. The bromination reaction did not occur at 200°C; this finding is contrary to the work of Grant (1). Unfortunately, the particle size of Grant's samples was not stated.

In an experiment designed to assess the extent of the recovery of dissolved oxygen in titanium as TiO_2 , using bromination, titanium turnings were heated in oxygen to produce a blue oxide film. Bromination of this material, as shown in Table 3, indicated that the added oxygen was not volatilized.

TABLE 3
Recovery of Oxygen Added to Titanium Turnings

Added		Found		
O_2 Added %	Equiv. TiO_2 %	Total Residue %	Residue %	TiO_2 (difference) %
0.31	0.77	1.24	0.48(a)	0.76

NOTE: (a) Average of the last three recorded values in Table 2, Column 4.

Thorium metal was received in lump form and, although the surface appeared to have an oxide coating, it was not cleaned prior to bromination. The reaction was as shown in Eq. 5:



The residue should contain ThBr_4 and a small amount of ThO_2 , which is proportional to and resulted from the oxygen in and on the thorium sample. The results shown in Table 4 are calculated as a percentage of the original weight.

TABLE 4
Bromination of Thorium

Bromination Temperature (°C)	Starting Weight	Gain in Weight	Calculated Formula	% Total Residue	% Methanol-Insol.
380	0.6678 g	0.7508 g	ThBr _{3.27}	212.43 ^(a)	23.3 ^(b)
500	0.6160 g	0.4724 g	ThBr _{2.23}	176.69 ^(a)	34.5 ^(c)

- NOTES: (a) These products were very unstable and gained weight steadily, even in a desiccator. This change is probably caused by water-addition and/or oxygen-addition reactions.
- (b) In this case, the residue was treated with methanol immediately after cooling and weighing.
- (c) This residue was stored in a desiccator for 14½ hours (gain = 0.1215 g) prior to methanol treatment. The methanol filtrate was found to contain 0.3582 g Th and 0.3938 g Br.

It is evident from Table 4 that the bromination of thorium metal did not yield a product that was stable with respect either to high temperature or to atmospheric conditions at room temperature.

In the case of the lower temperature (380°C), a calculation based on a thorium balance and the weight changes indicated that methanol probably dissolved ThBr₄ from ThO₂. However, the quantity of thorium and bromine found in the methanol filtrate of the residue obtained at 500°C indicated a ratio of Th:Br of 1:3.19 and, since their sum did not equal the methanol-soluble factor, the formation of an intermediate compound appears possible.

Two conclusions to be reached from the above discussion appear to be, firstly, that the residue, which contains ThBr₄, is thermally stable at about 380°C; and, secondly, that in order to avoid atmospheric reactions the ThBr₄ should be removed from the residues with methanol at the earliest opportunity.

The (titanium + 2.2% thorium) alloy was submitted as turnings and, in all cases, the bromination was made at 400°C. The extent of bromination and the results of analyses are shown in Table 5.

TABLE 5

Bromination of (Ti + 2.2% Th) Alloy

Surface Treatment	% Residue	% Methanol Insol.
None	3.34 ^(a)	2.93 ^(c)
None	4.47	1.25
Isopropyl ether	3.23 ^(a, b)	--

NOTES: (a) X-ray diffraction analysis indicated the presence of poorly crystalline ThO₂.

(b) X-ray fluorescence analysis indicated the presence of Th and Br but no Ti.

(c) Methanol filtrate contained 0.0022 g Br.

The physical analyses indicated that all the oxygen in the sample was either combined with the thorium or, if present as oxygen in solid solution, had combined, during the bromination, preferentially with the thorium rather than with the titanium. Thermodynamic data show ThO₂ to be more stable than TiO₂.

The (titanium + 2.5% ThO₂) alloy was received at the beginning of the experimental study and, due to this availability, it was used in more experiments than the other samples. The results of the bromination and analyses are shown in Table 6. Three observations concerning these results can be made:

- (a) Both Th and Br were found in the methanol filtrates but showed no fixed ratio, nor were they present in sufficient amounts to give a good weight balance.

TABLE 6

Bromination of (Ti + 2.5% ThO₂) Alloy

Form of Sample	Surface Treatment	Bromination Temperature (°C)	% Residue	% Methanol Insol.	% Thorium	% Bromine
Massive	Methanol	200	99.42			
Massive	Etchant	400	91.82			
Massive	Etchant	400	92.01			
Turnings	None	200	100.00			
Turnings	None	300	22.60			
Turnings	None	377	4.08	3.61	0.43	0.43
Turnings	None	400	4.31	2.68	--	0.64
Turnings	None	400	4.65	3.03	--	1.09
Turnings	None	350	9.81			
		360	4.53 ^(a)			
		400	4.37 ^(a)			
		500	2.93 ^(a, b)			
Turnings	Methanol	500	3.84	3.30	0.22	0.42
Turnings	Isopropyl Ether	400	4.23 ^(c)	2.66	0.81	0.62
Turnings	Isopropyl Ether	400	4.66			
		500	3.52 ^(a, d)			

NOTES:

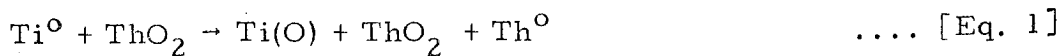
- (a) Additional bromination.
 (b) X-ray diffraction analysis indicated the presence of rutile + thorium dioxide.
 (c) X-ray diffraction analysis indicated the presence of thorium dioxide.
 X-ray fluorescence analysis indicated the presence of Th, Br, with a little Ti.
 (d) X-ray diffraction analysis indicated the presence of thorium dioxide.
 X-ray fluorescence analysis indicated the presence of Th, Br, but no Ti.

- (b) X-ray fluorescence analysis of the residue confirmed the presence of Br and Th in approximately the same ratio as by chemical analysis, which was sufficient for some ThBr_4 to be present in amounts equalling about one-quarter of the residue. However, little or no titanium was detected.
- (c) X-ray diffraction analysis did not show the presence of any bromides but, since only crystalline materials are detected by this procedure, any amorphous substance would remain undetected unless present in a predominant amount.

The interpretation of these results, even in the light of the observations from previous samples, is neither easy nor conclusive. A plausible explanation appears to be that, firstly, the ThO_2 found in the residues had absorbed varying amounts of bromine, with the possibility of a complex having been formed, and the bromine, although removed slowly with increasing temperature, is not completely driven off even at 500°C ; and, secondly, when the residue is leached with methanol, some of the suggested thorium/bromine complex is perhaps dissolved along with the bromine.

CONCLUSIONS

There appears to be no evidence that the following reaction is occurring during the preparation of the $(\text{Ti} + 2.5\% \text{ThO}_2)$ alloy:



as the concentration of titanium appears to be extremely low in all the residues.

The confirmational approach, based on the absence of ThBr_4 in the residue, could not be established.

It has been observed that the bromination technique yields a residue composed of hollow shells; that is, the surface oxide film appears to be isolated intact, with the central metallic core largely removed, leaving a small internal residue. It is thought probable that this technique might be useful for isolating these surface films for various studies.

Another logical outcome from this study appears to be that a method of determining the solid state oxygen in titanium could be developed. The proposed method would be based on the proper assessment of results obtained from the bromination of titanium by the method of this report to obtain total oxygen content, and results from the methanol-bromine reflux method (2), which was shown to be useful in isolating non-metallics, e.g. titanium oxides, from metallic titanium and oxygen-titanium solid solutions.

ACKNOWLEDGEMENTS

The author wishes to thank Mr. E. J. Murray, technician, Crystal Structure Group, for the X-ray diffraction analyses; and Mrs. D. J. Reed, research scientist, and Mr. J. L. Dalton, scientific officer, of the Spectrochemistry Section, for the X-ray fluorescence analyses. All the above-mentioned personnel are members of the Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa.

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- (1) Nicholas J. Grant, "Method of Producing Dispersion-Hardened Titanium Alloys", United States Patent No. 3,070,468; patented Dec. 25, 1962.
- (2) L. G. Ripley, "Analysis of Titanium and its Alloys", Research Report MD 143, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada, May 1, 1953.

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APPENDIX

The Methanol-Bromine Reflux Method

In a previous report (2), it was shown that a methanol-bromine reflux reaction would dissolve the oxygen in solid solution in titanium, leaving no residue. Therefore, this procedure would isolate titanium and thorium oxides, which could then be collected by filtration; it was accepted that the particle size of the ThO_2 and the TiO_2 present in the samples of this project might be smaller than the pore-size of the filtering frit and, in this way, some insoluble particles would be lost in filtration.

However, each of the submitted samples was brominated in methanol at refluxing temperature and the results are shown in Table 7. These results are submitted for comparison only, and NO attempt has been made to analyse these residues.

TABLE 7

Bromine-Methanol (Refluxing) Residues

Sample	Form of Sample	% Residue (after filtration)
Ti	Massive	0.62 (incomplete
Ti	Turnings	0.14 bromination)
Th	Massive	6.09
(Ti + 2.2% Th)	Turnings	0.41
(Ti + 2.5% ThO_2)	Massive	0.32
(Ti + 2.5% ThO_2)	Turnings	0.23

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Ottawa, June 1970

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