63-3-2



ARL 63-13



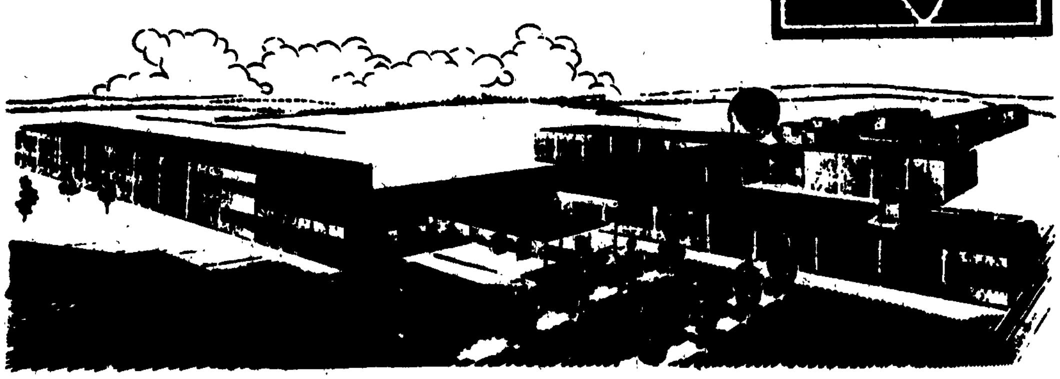
# METHOD FOR DETERMINATION OF THE FREE AND TOTAL TITANIUM CONTENTS IN $ZrO_2$-Ti COMPOSITIONS

ROSS W. MOSHIER
CHEMISTRY RESEARCH LABORATORY

ROBERT RUH
METALLURGY AND CERAMICS RESEARCH LABORATORY

JANUARY 1963

AERONAUTICAL RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE



## NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

. . . . . . . . . .

Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency, (ASTIA), Arlington Hall Station, Arlington 12, Virginia.

. . . . . . . . . .

This report has been released to the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C. for sale to the general public.

. . . . . . . . . .

Copies of ARL Technical Documentary Reports should not be returned to Aeronautical Research Laboratory unless return is required by security considerations, contractual obligations, or notices on a specific document.

AF-WP-L-APR 63 100

24-570, 300, 4-11-63

Aeronautical Research Laboratories, Wright-Patterson AFB, O. METHOD FOR DETERMINATION OF THE FREE AND TOTAL TITANIUM CONTENTS IN $ZrO_2$-Ti COMPOSITIONS by Ross W. Moshier, Robert Ruh, of ARL. January 1963. 14 p. incl. illus. tables. (Project 7022;Task 7022-02)
(ARL 63-13) Unclassified Report

Procedures have been developed for the determination of the total titanium content and the free titanium content by chemical analysis. Using these procedures the amounts of total titanium and free titanium have been determined in $ZrO_2$-Ti compositions with 0.38, 1.2, 2.0, and 6.4 weight % Ti. With this data it has been possible to determine the stability

( over )

UNCLASSIFIED

UNCLASSIFIED

Aeronautical Research Laboratories, Wright-Patterson AFB, O. METHOD FOR DETERMINATION OF THE FREE AND TOTAL TITANIUM CONTENTS IN $ZrO_2$-Ti COMPOSITIONS by Ross W. Moshier, Robert Ruh, of ARL. January 1963. 14 p. incl. illus. tables. (Project 7022;Task 7022-02)
(ARL 63-13) Unclassified Report

Procedures have been developed for the determination of the total titanium content and the free titanium content by chemical analysis. Using these procedures the amounts of total titanium and free titanium have been determined in $ZrO_2$-Ti compositions with 0.38, 1.2, 2.0, and 6.4 weight % Ti. With this data it has been possible to determine the stability

( over )

UNCLASSIFIED

UNCLASSIFIED

of the titanium when present in the free state and in solid solution. Results of the total titanium analysis have revealed that there is no significant loss of titanium at any firing temperature when the titanium is in solid solution in zirconia. Above the solubility limit, vaporization of the free titanium begins at 1500°C. and the rate increases with temperature. Results of the free titanium analyses have showed that there is virtually no free titanium in compositions below the solubility limit. They also have given the amount of free titanium in compositions above the solubility limit. A combination of the data of both analyses has revealed the amount of titanium in solid solution in zirconia.

UNCLASSIFIED

UNCLASSIFIED

of the titanium when present in the free state and in solid solution. Results of the total titanium analysis have revealed that there is no significant loss of titanium at any firing temperature when the titanium is in solid solution in zirconia. Above the solubility limit, vaporization of the free titanium begins at 1500°C. and the rate increases with temperature. Results of the free titanium analyses have showed that there is virtually no free titanium in compositions below the solubility limit. They also have given the amount of free titanium in compositions above the solubility limit. A combination of the data of both analyses has revealed the amount of titanium in solid solution in zirconia.

UNCLASSIFIED

UNCLASSIFIED

ARL 63-13

# METHOD FOR DETERMINATION OF THE FREE AND TOTAL TITANIUM CONTENTS IN $ZrO_2$-Ti COMPOSITIONS

ROSS W. MOSHIER
CHEMISTRY RESEARCH LABORATORY

ROBERT RUH
METALLURGY AND CERAMICS RESEARCH LABORATORY

JANUARY 1963

PROJECT 7022
TASK 7022-02

AERONAUTICAL RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

## FOREWORD

This interim technical report was prepared by Dr. Ross Moshier, Chemistry Research Laboratory, and Dr. Robert Ruh, Metallurgy and Ceramics Research Laboratory of the Aeronautical Research Laboratories, Office of Aerospace Research, United States Air Force. The work reported herein was accomplished on Task 7022-02, "Bonding in Metal-Ceramic, Ceramic, and Intermetallic Systems" of Project 7022, "Surface and Interface Phenomena of Matter."

## ABSTRACT

Procedures have been developed for the determination of the total titanium content and the free titanium content by chemical analysis. Using these procedures the amounts of total titanium and free titanium have been determined in $ZrO_2$-Ti compositions with 0.38, 1.2, 2.0 and 6.4 weight % Ti. With this data it has been possible to determine the stability of the titanium when present in the free state and in solid solution. Results of the total titanium analysis have revealed that there is no significant loss of titanium at any firing temperature when the titanium is in solid solution in zirconia. Above the solubility limit, vaporization of the free titanium begins at 1500°C, and the rate increases with temperature. Results of the free titanium analyses have showed that there is virtually no free titanium in compositions below the solubility limit. They also have given the amount of free titanium in compositions above the solubility limit. A combination of the data of both analyses has revealed the amount of titanium in solid solution in zirconia.

## TABLE OF CONTENTS



## LIST OF ILLUSTRATIONS

# I. INTRODUCTION

The purpose of the present work was to develop chemical analyses for Ti in fired $ZrO_2$-Ti compositions, which would reveal (1) the total Ti content and, therefore, the vaporization loss of Ti, and (2) the amount of free Ti, thus making possible a determination ot the Ti in solid solution. The vaporization loss would be the starting Ti content minus the fired Ti content. The amount of Ti in solid solution would be the difference between the total Ti content and the free Ti content tor fired samples.

The chemical analyses data were desired to supplement an earlier investigation, one part of which determined the amount and type of Ti solid solution in $ZrO_2$ (Ref 1). In the earlier work, results of weight change and bulk density determinations, metallographic and petrographic analyses, and electron probe analyses revealed that 1.6 weight % Ti is retained as a substitutional solid solution in $ZrO_2$. These analyses were made on samples which had been fired in vacuum in the temperature range 1200 - 2000°C.in vacuum. While there was good agreement in the findings of these different analyses, another determination was desired.

# II. DEVELOPMENT OF THE PROCEDURE

## (1) TOTAL TITANIUM ANALYSIS

### (a) Discussion

The analysis of a material for total titanium can be accomplished most advantageously by a volumetric method. Rahm (Ref 2) discusses the relative merits of the reduction of titanium (IV) to titanium (III) by use of the Jones Reductor, and by use of metallic aluminum. In his recommended procedure he titrates the titanium

(III) with a standard solution of ferric ion using a thiocyanate end point, and gives data to prove the superiority of this method. It is surprising that such good results were obtained, because in his procedure he does not give any precautions for preventing air oxidation of the titanium (III) subsequent to reduction and during the titration. The procedure adopted was that given by Scott (Ref 3) because of detailed precautions cited, and because in the $ZrO_2$-Ti compositions there are no ions present which would interfere in the reduction and titration of the reduced specie.

(b) Procedure for Total Titanium

Crush the sample and grind it in a boron carbide mortar to a powder, 80-100 mesh, and store the sample in a weighing bottle. When both total titanium and free titanium metal are to be determined, the sample must be ground to pass 400 mesh as described in procedure for free titanium.

Weigh 0.05 to 0.10g. samples into 30-ml. platinum crucibles. Add 10 ml. of 48% hydrofluoric acid to each crucible and place them on a low-temperature hot plate and cover the crucibles. Fill the depression in the covers with water to minimize loss of acid during the dissolution of the samples. The liquid should not boil during the digestion. Samples usually require 30-60 minutes for complete dissolution.

When dissolution of the samples is complete, rinse the crucible covers with a jet of distilled water receiving the rinsings in the crucibles. Add 10 ml. of 50% sulfuric acid to each crucible and evaporate until copious fumes of sulfuric acid are evolved. Transfer the sample solutions to 400-ml. beakers which contain 10 ml. of 50% sulfuric acid. Rinse the crucibles with distilled water, policing them between each rinsing, and receiving the rinsings in the beakers. Dilute the solutions to 100-ml. volume with boiled distilled water.

Prepare a Jones Reductor with 20-30 mesh amalgamated zinc and keep it filled with distilled water when not in use. The amalgamated zinc in the reductor should be renewed when its appearance becomes a dull grey color.

In order to reduce the sample the following procedure is used. Activate the Jones Reductor by passing through it 100 ml. of hot freshly boiled 5% sulfuric acid. Prepare a receiver from a 500-ml. filtering flask, with stopper containing inlet and outlet tubes for carbon dioxide gas, and a long tube reaching to the bottom for attachment to the Jones Reductor outlet. Place 25 ml. of 3 M ferric alum solution in the flask. Attach the flask to the Jones Reductor and flush it with carbon dioxide. With a slow stream of carbon dioxide passing through the flask, add the sample solution to the Jones Reductor and receive the eluate under the surface of the alum solution. Rinse the beaker several times using a total of 100 ml. of boiled 5% sulfuric acid, and pass the rinsings through the reductor. Finally pass 50 ml. additional boiled 5% sulfuric acid through the reductor.

Transfer the cooled alum solution to a 400-ml. beaker. Rinse the tubes and filtering flask with 5% sulfuric acid and add the rinsings to the beaker. Add 3 ml. of 85% ortho-phosphoric acid to the solution. Titrate the solution with 0.05 N potassium permanganate solution potentiometrically using a platinum indicating electrode, and a saturated calomel electrode as a reference.

Run a blank on all the reagents, carrying the blank through the entire procedure, and obtain the titration blank. Subtract the titration blank from the sample titer to obtain the net titration for the sample in milliliters. One ml. of 0.05 N potassium permanganate is equivalent to 2.371 mg. titanium.

## (2) FREE TITANIUM ANALYSIS

### (a) Discussion

For the determination of free titanium metal in the $ZrO_2$-Ti compositions the method of Straumanis, Cheng and Schlecten (ref 4) was considered. The method consists in measuring the evolved hydrogen gas generated by dissolution of the metal in hydrofluoric acid. Oxides of titanium also dissolve in this procedure. Because titanic ions resulting from solution of titanium (IV) in the $ZrO_2$-Ti composition will react with titanium metal without hydrogen evolution, it was realized that results would be in error. Therefore, it was necessary to develop a new method.

Pure titanium metal, pure titanium dioxide, pure zironia and a representative $ZrO_2$-Ti composition were subjected to dissolution study in sulfuric acid. The variables were acid concentration, temperature and time. The optimum conditions found were dissolution in 6 N sulfuric acid in a constant temperature bath held at 85°C. for a 30 minute period. Under these conditions, pure titanium metal dissolved completely when alone, and when mixed with titanium dioxide. Pure titanium dioxide did not dissolve at all when alone or when mixed with pure titanium metal and pure titanium dioxide. Replicate analyses of the representative $ZrO_2$-Ti composition sample gave reproducible results for free titanium metal.

### (b) Procedure for Free Titanium

Crush and grind the material in a boron carbide mortar to pass 400 mesh. Store the sample in a weighing bottle.

Accurately weigh out 0.4000 to 0.5000 g. samples placing them in 250-ml. beakers with covers. Pre-heat 6 N sulfuric acid to 85°C. and add 50 ml. to each of the samples in the beakers. Place the covered beakers in an 85°C. thermostated water bath and allow to digest for 30 minutes. Remove from the bath and filter on Whatman No. 42 filter paper. Wash the beaker and decant the washings on to the filter using 5% sulfuric acid. Wash the filter four times with this acid. The combined filtrate and washings should be about 1000 ml. in volume.

From here on follow the procedure for total titanium beginning with the reduction of the sample.

(3) APPARATUS AND REAGENTS

(a) Apparatus

Constant temperature bath

Jones Reductor

Potentiometric titrator with platinum metal and saturated calomel electrodes

30 ml. platinum crucibles

400 ml. beakers

500 ml. suction flasks

Boron carbide mortar and pestle

Magnet

Wash bottles

(b) Reagents

Hydrofluoric acid, 48%

Distilled water, boiled free from dissolved air

Sulfuric acid, d 1.84

Sulfuric acid, 50% by volume

Sulfuric acid, 5% by volume

Sulfuric acid, 6 N

Zinc, 20-30 mesh (low in iron).

Mercuric chloride, 5% solution

Ferric ammonium alum, 3 M solution in 8% sulfuric acid by volume. Use boiled acid solution and keep under an inert atmosphere.

Carbon dioxide, in cylinder

Ortho-phosphoric acid, 85%.

Potassium permanganate solution 0.05 (Standardized with Bureau of Standards certified sodium oxalate.)

Titanium metal powder, pure.

Titanium dioxide, pure

Zirconia, pure

## III. EXPERIMENTAL DATA

### (1) TOTAL TITANIUM

The compositions which were analyzed for total titanium, together with their firing treatment and the results obtained, are given in Table I. All compositions are in Weight %. Two or more separate determinations were made in each case. The first part of this data is presented in Figure 1 where the total titanium content of different compositions is plotted against the starting composition. The second part of the data is presented in Figure 2 where the total titanium content is plotted against firing temperature.

## (2) FREE TITANIUM

The compositions which were analyzed for free titanium together with firing treatment and the results obtained are given in Table II. As in the previous analysis, two or more determinations were made in each case. These data are presented in Figure 3 where the free titanium content after firing is plotted against the starting composition.

TABLE I

TOTAL TITANIUM ANALYSIS OF $ZrO_2$-$T_i$ COMPOSITIONS

| No. | Composition | Firing Treatment | Titanium Content (%) 1st 2nd 3rd 4th | Average |
|---|---|---|---|---|
| 1 | $ZrO_2$ | Raw Material | 0.00, 0.00 | 0.0 |
| 2 | $ZrO_2$ | 2000°C/2 hr. | 0.167, 0.137 | 0.15 |
| 3 | $ZrO_2$+ 0.38%Ti | 2000°C/2 hr. | 0.252, 0.270 | 0.26 |
| 4 | $ZrO_2$+ 1.2% Ti | 2000°C/2 hr. | 0.912, 1.08, 1.07 | 1.0 |
| 5 | $ZrO_2$+ 2.0%Ti | Raw Material | 2.10, 2.14, 2.20 | 2.1 |
| 6 | $ZrO_2$+ 2.0%Ti | 2000°C/2 hr. | 2.34, 2.18, 2.21 | 2.2 |
| 7 | $ZrO_2$+ 6.4%Ti | Raw Material | 5.80, 5.87 | 5.8 |
| 8 | $ZrO_2$+ 6.4%Ti | 2000°C/2 hr. | 4.33, 4.57, 4.63 | 4.5 |
| 9 | $ZrO_2$+ 6.4%Ti | 1900°C/2 hr. | 4.53, 4.63 | 4.6 |
| 10 | $ZrO_2$+ 6.4%Ti | 1800°C/2 hr. | 4.78, 4.65 | 4.7 |
| 11 | $ZrO_2$+ 6.4%Ti | 1700°C/2 hr. | 5.25, 5.15, 5.25, 5.20 | 5.2 |
| 12 | $ZrO_2$+ 6.4%Ti | 1600°C/2 hr. | 5.14, 5.49 | 5.3 |
| 13 | $ZrO_2$+ 6.4%Ti | 1500°C/2 hr. | 5.95, 5.89 | 5.9 |

## TABLE II

### FREE TITANIUM ANALYSIS OF $ZrO_2$-Ti COMPOSITIONS

| No. | Composition | Firing Treatment | Titanium Content (%) 1st 2nd 3rd 4th | Average |
|---|---|---|---|---|
| 1 | $ZrO_2$ | 2000°C./2 hr. | 0.00, 0.0221 | 0.011 |
| 2 | $ZrO_2$+ 0.38%Ti | 2000°C./2 hr. | 0.0665, 0.0493 | 0.058 |
| 3 | $ZrO_2$+ 1.19%Ti | 2000°C./2 hr. | 0.0882, 0.0588 | 0.074 |
| 4 | $ZrO_2$+ 2.00%Ti | 2000°C./2 hr. | 0.197, 0.192, 0.160, 0.148 | 0.17 |
| 5 | $ZrO_2$+ 6.42%Ti | 2000°C./2 hr. | 3.03, 3.16, 3.05, 3.07 | 3.1 |

## IV. DISCUSSION OF RESULTS

It is seen from Table I and Figure 1 that there is no significant lost of titanium for compositions up to 2% Ti. This is reasonable since they are below or slightly above the solubility limit. The 6.4% Ti composition, in contrast, is considerably above the solubility limit and vaporization of some of the free titanium occurs. Thus, there is only 5.8% Ti in this sample. One inconsistency observed is that the 2.0% composition fired to 2000°C./2 hr. contains more titanium than the starting composition. This is believed due to titanium pickup from the furnace. (The same effect is noted in the 6.4% Ti sample fired to 1500°C./2 hr.) The disagreement between analyses of raw batches and the compositions sought in the weighings probably was due to the mixing procedure.

The rate of vaporization of titanium in the 6.4% Ti composition above the solubility limit is illustrated in Figure 2. Here it is seen that there is no loss of titanium at 1500°C., but that when the firing temperature is increased, the loss increases continuously.

In Figure 3 it is seen that there is essentially no free titanium in the 0.38 and 1.2% compositions. The 2.0% composition has a very small amount while the 6.4% composition has a considerable amount. Thus, the solid solubility is indicated by this data also. The fact that Ti is lost through vaporization is illustrated by the free Ti line showing a lesser slope than the starting composition line.

Comparison of the free Ti analysis data with the total Ti analysis data reveals the following amounts of solid solution for different compositions fired to 2000°C/2hr.

| Composition | Solid Solution Titanium |
|---|---|
| $ZrO_2$+ 0.38%Ti | 0.2 |
| $ZrO_2$+ 1.2%Ti | 1.0 |
| $ZrO_2$+ 2.0%Ti | 2.1 |
| $ZrO_2$+ 6.4%Ti | 1.4 |

The first and second results are somewhat low, probably due to vaporization before solid solution took place. The third result is higher than the 1.6% solubility limit obtained by other methods of analysis and this difference is not explained. The fourth result is in good agreement with the 1.6% value.

## V. CONCLUSIONS

Results of the total titanium analyses have revealed that there is no significant loss of titanium at any firing temperature, when the titanium is in solid solution in zirconia. Above the solubility limit, vaporization of the free titanium begins at 1500°C and the rate increases with temperature.

Results of free titanium analyses have showed that there is virtually no free titanium in compositions below the solubility limit. They also have given the amount of free titanium in compositions above the solubility limit.

**A combination of the data of both analyses has revealed the amount of titanium in solid solution in zirconia.**

## BIBLIOGRAPHY


1. Robert Ruh, "Reactions of Zirconia and Titanium at Elevated Temperatures," J. Am. Ceram. Soc., in press.

2. Joseph A. Rahm, Anal. Chem. 24, 1832 (1952).

3. W. W. Scott, "Standard Methods of Chemical Analysis", 5th edition, D. van Nostrand Co., New York, 1939. pp. 984-5; 476; 986.

4. M. E. Straumanis, C. H. Cheng, and A. W. Schlechten, Anal. Chem. 28, 1883 (1956).

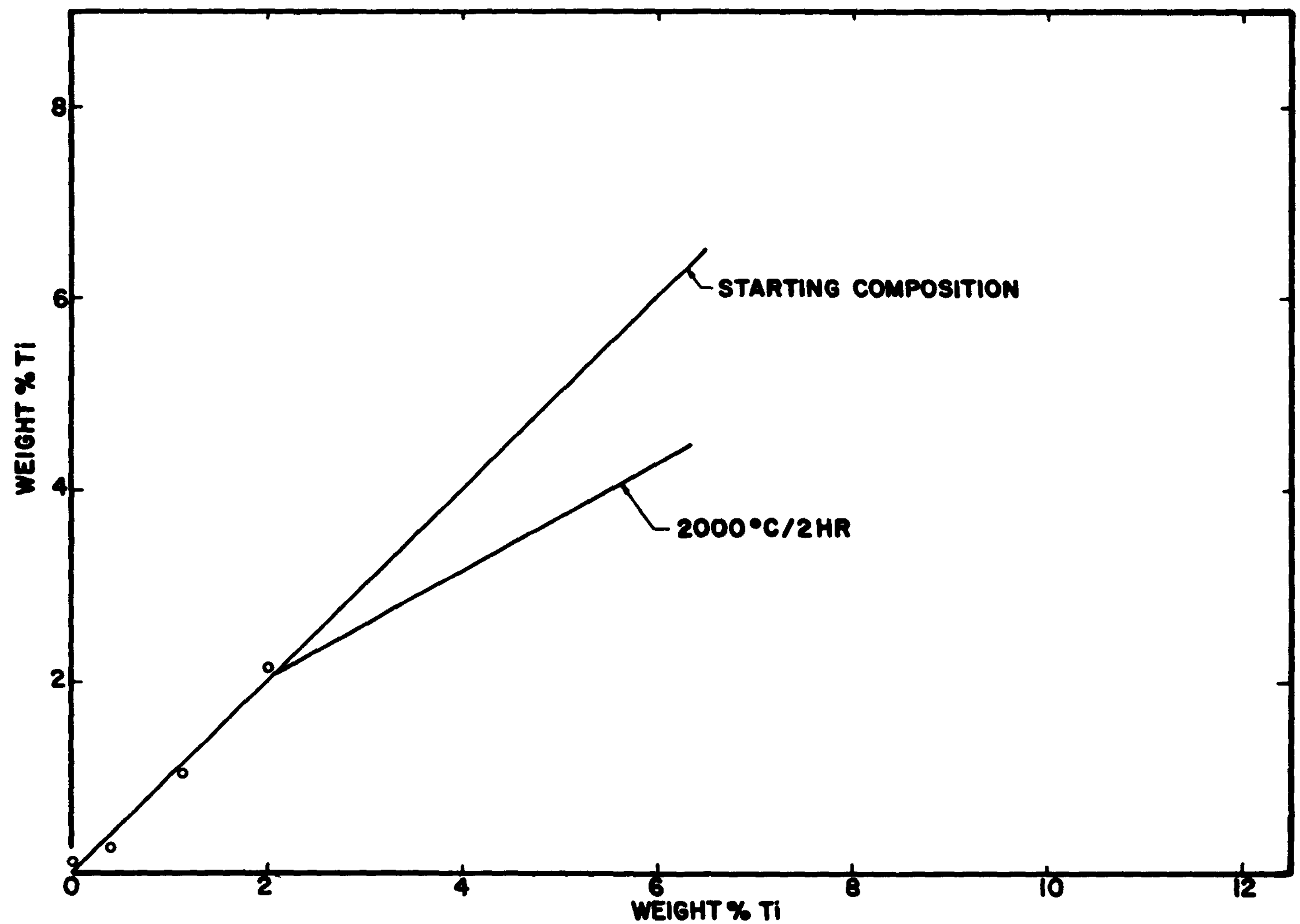



**Figure 1.** Total titanium content in $ZrO_2$-Ti composition after firing to 2000°C versus initial composition.

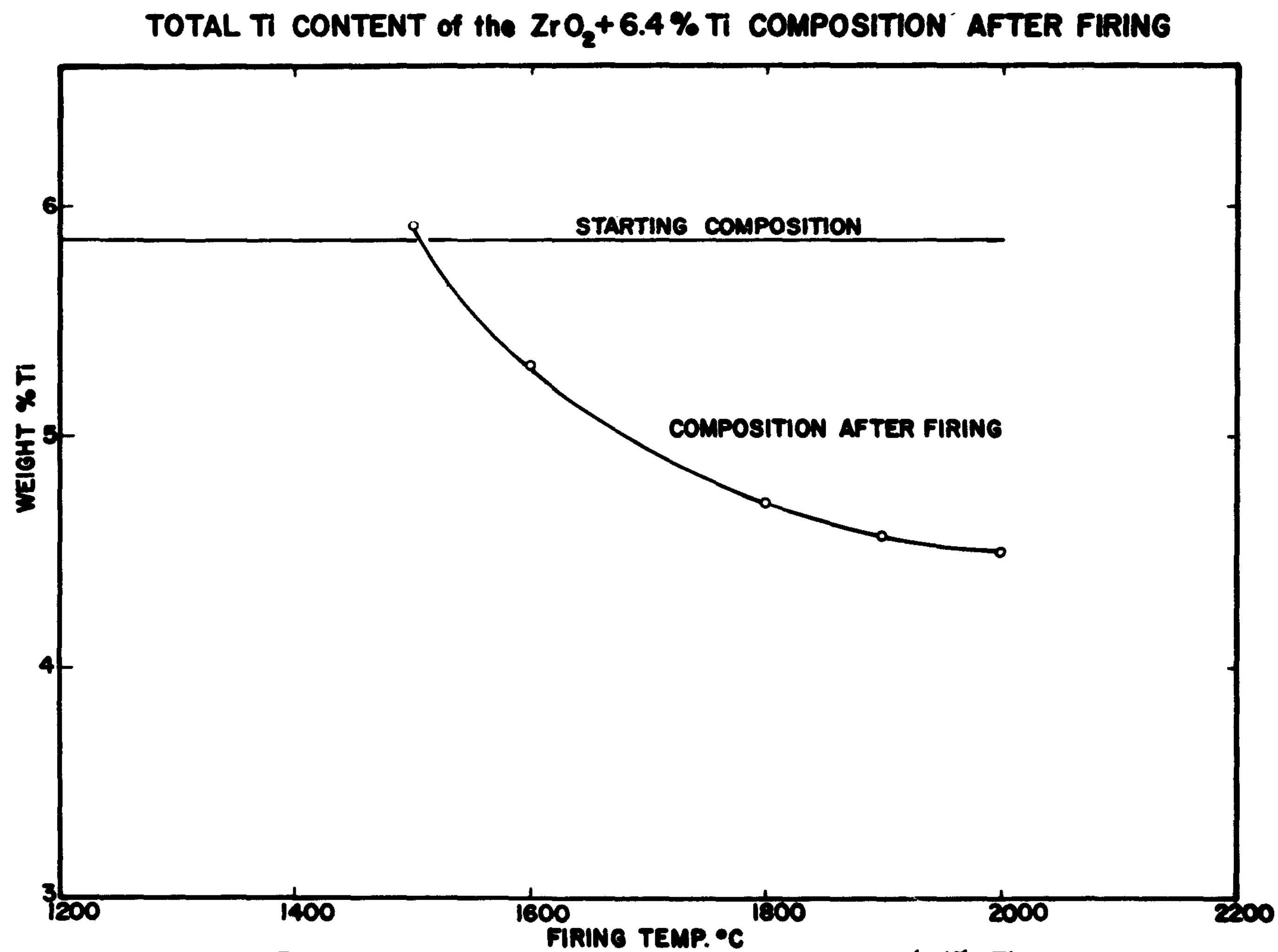



Figure 2. Total titanium content in the $ZrO_2$ + 6.4% Ti composition after firing to different temperatures.

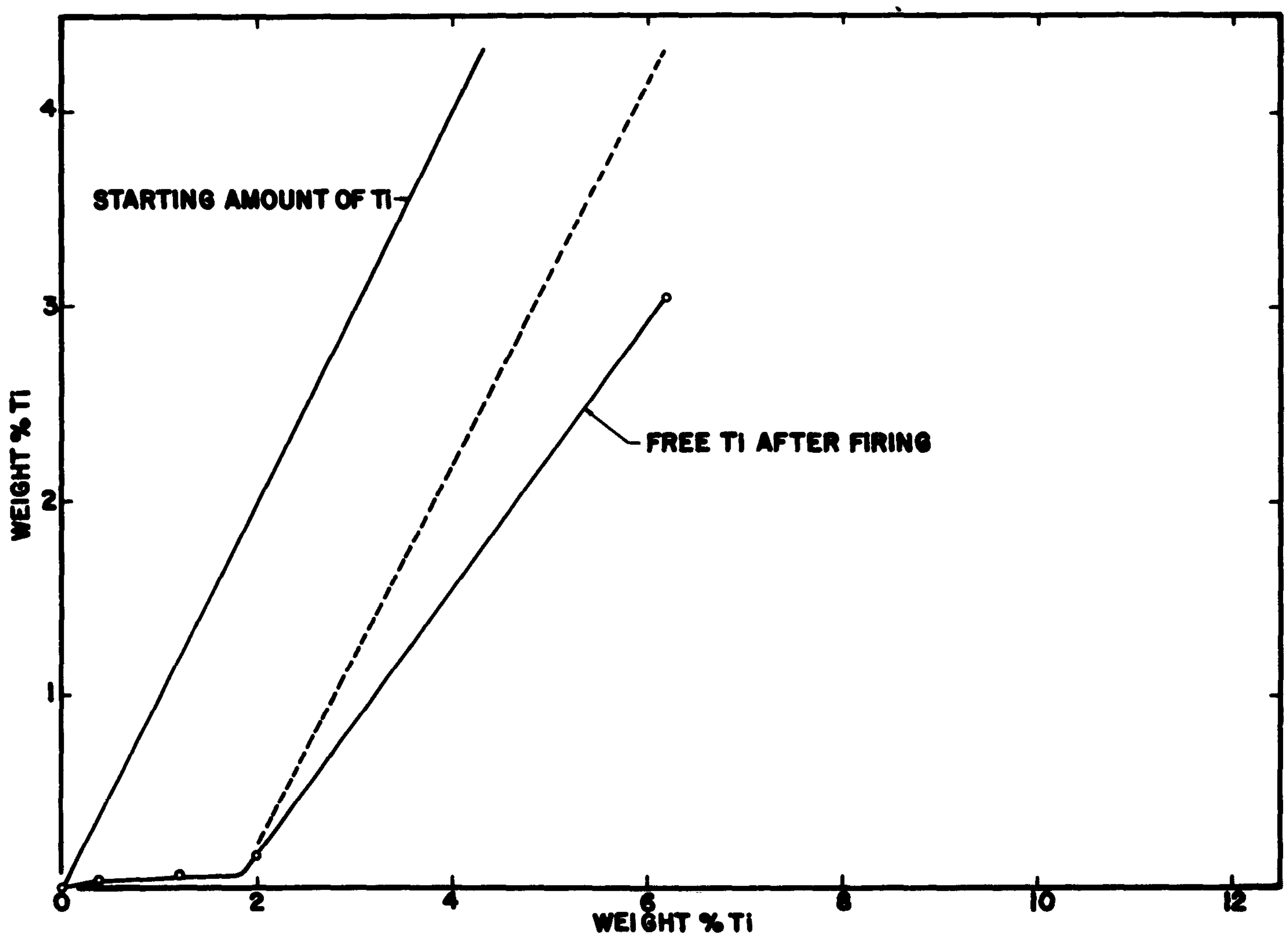



Figure 3. Free titanium content in $ZrO_2$-Ti compositions after firing to 2000°C versus initial composition.

Aeronautical Research Laboratories, Wright-Patterson AFB, O. METHOD FOR DETERMINATION OF THE FREE AND TOTAL TITANIUM CONTENTS IN $ZrO_2$-Ti COMPOSITIONS by Ross W. Moshier, Robert Ruh, of ARL. January 1963. 14 p. incl. illus. tables. (Project 7022;Task 7022-02)
(ARL 63-13) Unclassified Report
Procedures have been developed for the determination of the total titanium content and the free titanium content by chemical analysis. Using these procedures the amounts of total titanium and free titanium have been determined in $ZrO_2$-Ti compositions with 0.38, 1.2, 2.0, and 6.4 weight % Ti. With this data it has been possible to determine the stability

( over )

UNCLASSIFIED

UNCLASSIFIED

Aeronautical Research Laboratories, Wright-Patterson AFB, O. METHOD FOR DETERMINATION OF THE FREE AND TOTAL TITANIUM CONTENTS IN $ZrO_2$-Ti COMPOSITIONS by Ross W. Moshier, Robert Ruh, of ARL. January 1963. 14 p. incl. illus. tables. (Project 7022;Task 7022-02)
(ARL 63-13) Unclassified Report
Procedures have been developed for the determination of the total titanium content and the free titanium content by chemical analysis. Using these procedures the amounts of total titanium and free titanium have been determined in $ZrO_2$-Ti compositions with 0.38, 1.2, 2.0, and 6.4 weight % Ti. With this data it has been possible to determine the stability

( over )

UNCLASSIFIED

UNCLASSIFIED

of the titanium when present in the free state and in solid solution. Results of the total titanium analysis have revealed that there is no significant loss of titanium at any firing temperature when the titanium is in solid solution in zirconia. Above the solubility limit, vaporization of the free titanium begins at 1500°C. and the rate increases with temperature. Results of the free titanium analyses have showed that there is virtually no free titanium in compositions below the solubility limit. They also have given the amount of free titanium in compositions above the solubility limit. A combination of the data of both analyses has revealed the amount of titanium in solid solution in zirconia.

UNCLASSIFIED

UNCLASSIFIED

of the titanium when present in the free state and in solid solution. Results of the total titanium analysis have revealed that there is no significant loss of titanium at any firing temperature when the titanium is in solid solution in zirconia. Above the solubility limit, vaporization of the free titanium begins at 1500°C. and the rate increases with temperature. Results of the free titanium analyses have showed that there is virtually no free titanium in compositions below the solubility limit. They also have given the amount of free titanium in compositions above the solubility limit. A combination of the data of both analyses has revealed the amount of titanium in solid solution in zirconia.

UNCLASSIFIED

UNCLASSIFIED