MASTER

X-822

EXTERNAL TRANSMITTAL AUTHORIZED

OAK RIDGE NATIONAL LABORATORY

Operated by
UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation

Post Office Box X
Oak Ridge, Tennessee

ORNL
CENTRAL FILES NUMBER

59-5-77

COPY NO.

37

R-9405
DATE: May 19, 1959
SUBJECT: Determination of Thickness of Oxide
Film on Phosphor Bronze
TO: See Distribution
FROM: J. C. White

JCW-95

ABSTRACT

The thickness of an oxide film on phosphor bronze helices was determined by first establishing the oxygen content of the helix "as received" and after cleansing with nitric acid. Based on the assumption that the difference between these two values was the oxygen in the film, and that the film consisted entirely of cupric oxide, the thickness of the film was calculated from the density of cupric oxide, weight of film, and surface area of film. A value of 1080 Å was calculated as the thickness by this method.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

RELEASE APPROVED
BY PATENT BRANCH

1-11-61 *[Signature]*
DATE SIGNATURE

REVIEWED BY
PATENT OFFICE

5/17/59 *[Signature]*

8-1

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DETERMINATION OF THICKNESS OF OXIDE FILM ON PHOSPHOR BRONZE

J. C. White

Purpose

To determine the thickness of an oxide film on helices of phosphor bronze.

Introduction

Phosphor bronze helices are being used as packing materials for distillation columns in the chemical separation of oxygen isotopes. These helices have an average weight of 12.0 mg and an average surface area of 0.263 cm². It was desired to determine the thickness of the oxide film that is formed on these helices.

The proposed method of determining the thickness of the film was to: (1) determine the oxygen content of the helix as received, (2) immerse the helix in 1:20 nitric acid and determine the oxygen content of the cleaned sample. The difference in oxygen content is then the oxygen in the oxide film. To confirm this value, the sample was also heated in an hydrogen atmosphere at 300°C prior to the determination of the oxygen content. On the assumption that the difference in oxygen content is the oxygen in the oxide film, and that the film consists entirely of cupric oxide, its average thickness can then be calculated from the density of cupric oxide, weight of film, and surface area of film.

Experimental

The "as received" sample was washed with diethyl ether and dried for two hours at 110°C. Five helices, which weighed approximately 60 mg, were then taken for oxygen analysis, using the Leco inert gas fusion apparatus. The average value of three determinations was 550 ± 20 ppm of oxide. The coefficient of variation of the method, based on iron standards, is 5 per cent, so the order of precision was considered to be satisfactory. A second sample was then immersed in 1:20 nitric acid for 10 minutes, removed, washed with diethyl ether, and dried at 110°C in a helium atmosphere. The sample was then analyzed for oxygen as previously described. The average value for oxide was 250 ± 10 ppm. A third sample was heated in a hydrogen atmosphere at 300°C for one hour and then analyzed for oxygen as described above. The average value was 235 ± 10 ppm.

Calculation of Thickness of Oxide Film

- (1) Let A = Oxygen content of "as received" sample.
- (2) Let B = Average oxygen content of treated samples, assuming complete removal of oxide film.
- (3) Then, A - B = C, oxygen content of film.

$$550-245 = 305 \text{ ppm, or, } 0.0305 \text{ per cent}$$

$$(4) \text{ Average weight of helix } \times 0.0305 \text{ per cent } \times \frac{\text{Mol. wt. CuO}}{16} =$$

Weight of oxide as CuO, on an average helix, mg =

$$12 \times 0.000305 \times \frac{79.54}{16} = 0.0182 \text{ or } 18.2 \mu\text{g}$$

Surface area of average helix = 0.263 cm^2 .

Density of CuO = $6.4 \text{ g/cm}^3 = 6.4 \times 10^6 \mu\text{g/cm}^3$

Therefore: Thickness, cm = $\frac{\text{Wt. of film, } \mu\text{g}}{\text{Area, cm}^2 \times \text{Density, g/cm}^3}$

$$= \frac{18.2}{0.263 \times 6.04 \times 10^6}$$

$$= 10.80 \times 10^{-6}$$

$$\text{Thickness} = 1080 \text{ \AA}$$

Discussion

The validity of the calculation is directly dependent on two assumptions: (1) that the film is completely removed, or, its corollary, that only the film is removed, and (2) that the film consists of cupric oxide. The latter assumption is supported by Evans⁽¹⁾ who states that oxide coatings on copper greater than 400 Å thick are mainly cupric oxide. If the film were cuprous oxide, a corresponding calculation would yield 2070 Å, rather than 1080 Å. The excellent agreement between two different means of removing oxide film would lend credence to the assumption that the oxide film had been completely removed. It is also unlikely that the order of agreement achieved in this case would result if interstitial oxide had been removed.

Since the thickness of the CuO molecule is less than $3 \text{ \AA}$ in any plane, the calculated thickness represents a layer of some 350 molecules. If the film were cuprous oxide, the thickness would represent some 400 molecules.

This method would appear to be applicable to other metals and alloys where the oxide film can be readily removed.

Reference

1. U. R. Evans, Metallic Corrosion--Passivity and Protection, Edward Arnold and Co., London, p. 106, 1948.

J. C. White

Distribution

1. M. T. Kelley
2. C. D. Susano
3. J. C. White
4. J. S. Drury
5. Oscar Menis
6. L. J. Brady
7. A. S. Meyer, Jr.
8. J. A. Norris
9. H. P. House
10. J. R. Lund
11. C. K. Talbott
12. D. L. Manning
13. T. C. Rains
14. J. M. Peele
15. W. F. Vaughan
16. M. A. Marler
17. G. R. Wilson
18. L. T. Corbin
19. P. F. Thomason
20. S. A. Reynolds
21. G. W. Leddicotte
22. E. I. Wyatt
23. D. J. Fisher
24. C. Feldman
25. U. Koskela
26. W. R. Laing
27. C. E. Lamb
28. C. L. Burros
29. T. E. Willmarth
30. J. H. Cooper
31. D. E. LaValle
32. R. L. McCutchen
33. ORNL-RC
- 34-35. Laboratory Records
36. E. J. Murphy
37. M. J. Skinner

**DO NOT
PHOTOSTAT**