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CORROSION TEST PROCEDURE FOR THE
SELECTION OF CRYSTAL BAR ZIRCONIUM FOR USE
IN NAVAL REACTOR FUEL ELEMENTS

by
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May 10, 1950
and
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For The Atomic Energy Commission

H. F. Canale

Chief, Declassification Branch

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CORROSION TEST PROCEDURE FOR THE SELECTION OF CRYSTAL BAR ZIRCONIUM FOR USE IN NAVAL REACTOR FUEL ELEMENTS

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ABSTRACT

Reliable test equipment and a reproducible corrosion test procedure have been developed for the inspection and classification of crystal bar zirconium for naval reactor fuel elements. Every bar is examined and classified by a 168-hour high-temperature water corrosion test. This procedure has been instituted by ANL and is in use by the producers of crystal bar zirconium, the Foote Mineral Company.

Further investigations are in progress to develop a shorter selectivity procedure.

I. Introduction

The selection of corrosion-resistant crystal bar zirconium for use in the fabrication of fuel elements for the naval reactor is of prime importance, particularly for the fabrication processes which require compacting and extrusion. Earlier corrosion testing work has repeatedly demonstrated that the inclusion of one bar of noncorrosion-resistant zirconium in a compact has rendered it useless because of localized corrosion.

At first, small sections of zirconium crystal bar were used to evaluate corrosion resistance of an entire shipment. Poor corrosion resistance of compacts containing several lots from a shipment was traced, chemically and spectrochemically, to nonuniformity of material. Next, efforts were made to segregate corrosion-resistant lots of crystal bar by representative sampling. Duplicate samples of each lot in a shipment were subjected to a two-week static corrosion test at 600F in degassed distilled water. Again, the selection of good material could not be assured. Subsequent investigations determined a considerable variation in the composition between bars of a lot as well as along the length of individual bars. These preliminary corrosion data are summarized in the Naval Reactor Division Quarterly Report ANL-4424 and earlier quarterly reports.

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The uniformly unfavorable results of the first two procedures led to the decision to test all bars in each lot of a shipment. Since corrosion tests

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are time consuming, any reproducible and fairly rapid static qualitative test method which utilized visual inspection would be highly desirable. This short time test should correlate with standard quantitative corrosion evaluations.

II. Purpose

It is the purpose of this report to describe the most reliable and practical step-by-step inspection procedure developed and used by the Naval Reactor Division at the Argonne National Laboratory for the selection of corrosion-resistant zirconium. Later, this selective testing method was adopted as a regular test program at the Foote Mineral Company.

III. Test Equipment

Test equipment consists of a furnace and a special stainless steel autoclave. The furnace, Figure 1 (manufactured by the H. K. Huppert Company, Chicago, Illinois), is equipped to maintain a constant autoclave temperature during the test period.

The autoclave, Figures 2 and 3, consists of a threaded body, copper gasket, plug, and threaded nut. Early autoclaves, with the exception of the gasket, were fabricated from stainless steel type 347. Difficulty was experienced in opening these vessels after the test period, owing to metal seizure of the threads between the body and nut. Seizing was remedied by the substitution of a plain carbon steel plug and nut for the stainless counterparts. This modification resulted in corrosion of the carbon steel plug and the attendant contamination of the vessel contents. Corrosion of the steel plug and contamination were eliminated by the use of the original stainless steel type 347 plug. The final autoclave design has permitted duplication of hundreds of tests on zirconium.

Closure between the body and plug is effected by compression of the copper gasket by the threaded set screws in the top of the nut.

Interiors of new autoclaves are first degreased with trichloroethylene and then heated to 125F with 15-20 per cent nitric acid water solution for two hours. This hot nitric acid treatment produces a protective oxide layer.

Stainless steel type 347 was chosen as the material of construction for autoclaves after considering the following factors:

- A. Stainless type 347 has an extremely low corrosion rate in degassed distilled water at 600F (determined to be less than plus one-tenth (0.1) mg per square centimeter per month).

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- B. The potential difference between zirconium and a passivated stainless steel is very small. Preliminary work, using insulators to separate zirconium from the autoclave, showed variable corrosion of insulating materials under the conditions of the test. To eliminate the introduction of this variable contamination, it was decided to dispense with the use of insulating materials. Since the emf generated by the zirconium stainless steel couple is very small, a direct metal to metal contact would result in a negligible electrolytic attack.
- C. Type 347 stainless steel is now the first choice for the naval reactor vessel cladding. This permits an extended static study of the pressure vessel liner material over a long period of time under operating conditions similar to the final application.

IV. Test Procedure

The qualitative static corrosion test is conducted in accordance with the following conditions and procedures:

A. Test Conditions:

Temperature: 600F

Pressure: 1550 psi (equivalent saturation pressure)

Medium: Degassed single-distilled water

Exposure Time: 7 days (168 hours)

Internal Insulation: None

B. Crystal Bar Preparation and Autoclaving Procedure:

1. Degrease crystal bars by immersion in trichloroethylene for five (5) minutes.
2. Dry bars at 250F for one hour to remove solvent.
3. While bars are drying, prepare passivated autoclave for test by thorough washing with distilled water.
4. Insert new copper gasket into groove of autoclave shoulder. (Used gaskets may have taken permanent sets, and leaky joints may result.)
5. Place cleaned and dried crystal bars in autoclave.
6. Fill autoclave with cold single-distilled water to within three (3) inches of gasket. (Do not fill completely; sufficient volume must be provided for the expansion of water on heating from atmospheric temperature to 600F.)
7. Degas water in autoclave by boiling for five (5) minutes.
8. Immediately position stainless steel plug against copper gasket and screw nut down.
9. Force set screws down against plug to flow copper gasket, insuring a pressure-tight seal between autoclave body and nut.

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10. Place autoclave in furnace and maintain test temperature for 168 hours.
 11. After the exposure period has elapsed, remove autoclave from furnace and cool in running water until vessel is cool to the touch (to prevent steam and scalding water burns).
 12. After the autoclave has cooled, remove nut and plug.
 13. Remove bars and dry in an oven for one hour at 250F.
 14. Inspect bars visually.

C. Classification of Tested Bars:

For naval reactor use, the visually inspected bars will fall into three categories.

1. For compacting and extruding
2. For melting
3. Bad

Bars selected for compacting and extruding into cover plates for fuel elements must be uniformly coated with a very adherent iridescent surface tarnish with a total absence of visually detectable off-color corrosion products; for the melting process, bars may possess a very adherent iridescent surface tarnish mixed with spotty areas of dark gray corrosion products; bars classed bad are to include all material which shows large corroded areas characterized by dense surface or internal corrosion products. Zirconium from the first two classes only may be used as a source material for fuel element assemblies, depending on the fabrication process chosen. Zirconium falling into the third class is unsuitable for naval reactor applications.

A photograph which illustrates the various grades of crystal bar zirconium as they appear after completion of the static corrosion tests outlined in the procedure follows Figure 3.

- A. Bar 1 is in the "as received condition."
- B. Bar 2 is suitable for compacting or extrusion.
- C. Bars 3 and 4 are suitable for melting; note gray corrosion products near the ends and at the crystal boundaries of the respective samples.
- D. Bars 5, 6, and 7 are not suitable for use in the fabrication of naval reactor fuel plate assemblies. Bar 5 possesses a badly corroded surface and core; 6 shows a good core and a poor surface resistance; 7 has a good surface and poor core resistance.

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V. Summary

- A. Earlier procedures for the selection of corrosion-resistant crystal bar zirconium for fabrication of naval reactor fuel elements were found to be unreliable.
- B. The bar performance test outlined in this report sets up inspection and classification methods for the selection of corrosion-resistant crystal bar zirconium for use in naval reactor applications. It permits further classification of crystal bar zirconium as to use in a particular fabricating process, i.e., compacting, extrusion, or melting. This procedure is followed at the Foote Mineral Company, producers of crystal bar zirconium.
- C. This crystal bar performance test has provided a reproducible testing method for the selection of corrosion-resistant crystal bar zirconium for the fabrication of naval reactor fuel elements. Results leading to the adoption of this method are summarized in the Naval Reactor Division Quarterly Report ANL-4424 and the earlier quarterly reports.
- D. The performance test outlined in this report yields reliable information of corrosion resistance. A test duration period of 168 hours is not a rapid enough procedure for mass production usage. Faster methods for use as production control checks are under investigation.

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FIG. 1
AUTOCLAVE FURNACE

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FIG. 2
AUTOCLAVE COMPONENTS AND ASSEMBLY

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FIG.3
STATIC TEST AUTOCLAVE

SECTION **A-A**

MAXIMUM WORKING PRESSURE 2000 PSIG

TOLERANCE		AVERAGE PER CENT		STN.		GRADE		DATE		BY	
FRACTIONAL TOL.	1/2	EMPTY	1/2	FURNACE		FURNACE		FURNACE		FURNACE	
DECIMAL TOL.	0.005	EMPTY	0.005	FURNACE		FURNACE		FURNACE		FURNACE	
ANGLE	1/2	EMPTY	1/2	FURNACE		FURNACE		FURNACE		FURNACE	
ALL DIMENSIONS TO BE	1/2	EMPTY	1/2	FURNACE		FURNACE		FURNACE		FURNACE	
WITHIN TOLERANCE	1/2	EMPTY	1/2	FURNACE		FURNACE		FURNACE		FURNACE	
UNLESS OTHERWISE	1/2	EMPTY	1/2	FURNACE		FURNACE		FURNACE		FURNACE	
NOTED	1/2	EMPTY	1/2	FURNACE		FURNACE		FURNACE		FURNACE

FIG. 4

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Addendum to ANL-4450

July 19, 1950

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Corrosion Test Procedure for the Selection of Crystal Bar
Zirconium for Use in Naval Reactor Fuel Elements

Subsequent to the writing of this report, the Naval Reactor Division at Argonne and the Westinghouse Atomic Power Division have jointly established specifications for the base zirconium metal (crystal bar or BuMines unalloyed metal) to be supplied by the manufacturer which is used in the final step of making the sandwich type fuel plates for the Mark I Naval Reactor. These specifications (ANL-HE-576) differ from the corrosion test procedure presented herein as follows:

1. Time of Test - The time of the test period has been extended from one week (168 hours) to two weeks (336 hours). The specification states: "every piece of metal should be tested at 600F in degassed distilled water for two weeks."
2. Classification of Zirconium Metal After Test - The classification of "for melting" made visually on zirconium after test has been omitted. The specification states: "that metal which shows no white or gray deposit at the conclusion of the test is acceptable" (for fabrication by compacting, extruding or melting).

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