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CANNING GRAPHITE FOR GAS-COOLED REACTORS

by

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CANNING GRAPHITE FOR GAS-COOLED REACTORS

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A preliminary investigation was made of techniques and materials for canning graphite to protect it for use at high temperatures in a nitrogen-oxygen atmosphere.

Fabrication techniques for cladding bare and copper-plated graphite cores either in Type 316 stainless steel or Inconel X were developed. Specimens of the various combinations of core and cladding materials were subjected to simulated-service conditions and evaluated. In all cases the Type 316 stainless steel-clad specimens failed by carburization and subsequent oxidation in relatively short periods of time. Although considerable trouble was experienced with rupture in the vicinity of the cladding welds during thermal cycling of the Inconel X-clad specimens, this material appeared to be satisfactory in other respects and is considered promising.

A specimen of silicon-coated graphite clad with Type 316 stainless steel was tested by heat treating for 624 hr at 1800 F. The silicon coating alloyed with the cladding material, forming a high-silicon diffusion zone, but prevented carburization of the stainless steel.

INTRODUCTION

A massive UO_2-fueled graphite section has been considered as an advanced core concept for the GCRE. This section would be a right cylinder containing tubular coolant channels. These channels would be placed at the apexes of equilateral triangles to minimize hot spots in the element. Maximum estimated core-can interface temperature would be 1650 F. The coolant gas would probably be a nitrogen-oxygen mixture. At this temperature, fueled graphite must be canned to:

(1) Prevent oxidation of the graphite

(2) Provide structural stability

(3) Prevent release of fission gases.

Canning materials must:

(1) Carburize as little as possible

(2) Be resistant to nitriding

(3) Have good strength at elevated temperatures for an extended period of time.

A previous compatibility study(1) showed that nickel-base alloys containing titanium and/or aluminum, such as Inconel X, are relatively resistant to carburization and that a copper barrier layer minimizes the carburization of Type 316 stainless steel. On the basis of this compatibility study, both alloys were used with and without copper barrier layers in this investigation.

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Two tests were selected to evaluate the clad graphite assemblies. Thermal cycling between 480 and 1730 F was used to determine the extent of core cracking and the stability of all welds under cyclic conditions. Heat treatment at 1750 F for an extended period of time was used to determine the extent of internal carburization and external oxidation of the cladding materials.

MATERIALS AND CLADDING PROCEDURE

Materials

All cladding materials were used in commercially available gage thicknesses. Both Inconel X and Type 316 stainless steel were obtained in sheet form and sheared to the size required to form the containers. The Inconel X sheet was 0.031 in. thick and the Type 316 stainless steel stock was 0.030 in. thick. The tubing used for cladding the coolant channels measured 0.375 in. in OD with a 0.028-in. wall thickness. Headers were machined from a 3/16-in. plate.

Since this study was principally concerned with developing and testing fabrication techniques and cladding materials, nonfueled AGR or AGX graphite was used for the core material.

Electrodeposition of Copper on Graphite

Electrodeposition of copper on graphite was investigated and proved feasible. The cylinders were put into a jig (Figure 1) with Lucite or Teflon spacers holding 1/8-in.-diameter copper cathode rods in the centers of the coolant channels. The threaded corner-support rods and the copper support plates of the jig were coated with Grey Stonite.* The entire jig was then placed in absolute alcohol for 3 to 5 min before being transferred to the plating bath. The plating bath had a specific gravity of 1.175 and was a solution of the following:

	G per Liter
$CuSO_4 \cdot 5H_2O$	210
H_2SO_4	82.5
Molasses	2.5

A current density of 10 amp per ft^2 was used to plate the inside of the coolant channels whereas 20 amp per ft^2 was used to plate the outside of the cylinders. After plating the cylinders were reflux washed in distilled water for several hours and then baked at 500 F for 2 to 3 hr.

*A proprietary plater's masking lacquer manufactured by Stoner-Mudge, Inc.

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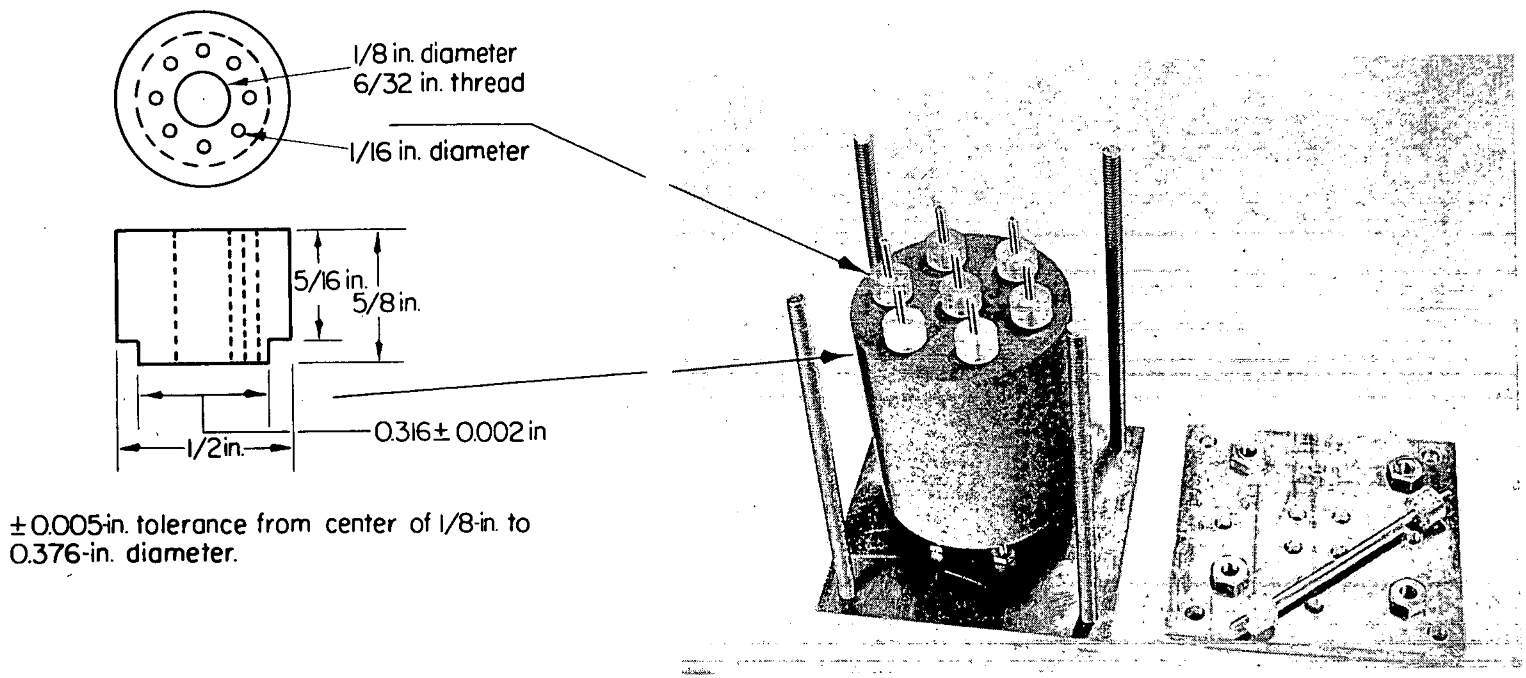

a.

Teflon Spacer for Holding and Positioning Copper-Rod Cathodes

b.

RM9523
A-29913

Graphite Cylinder in Jig

FIGURE 1. JIG FOR ELECTRODEPOSITION OF COPPER ON GRAPHITE

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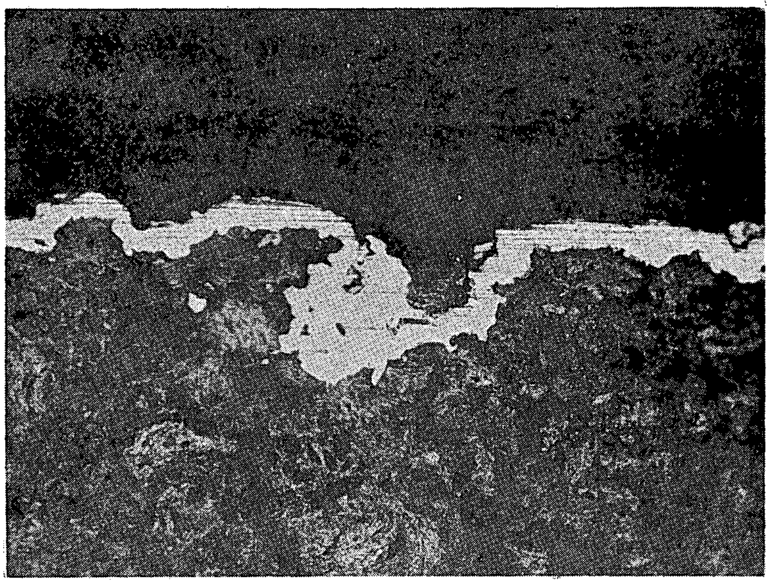
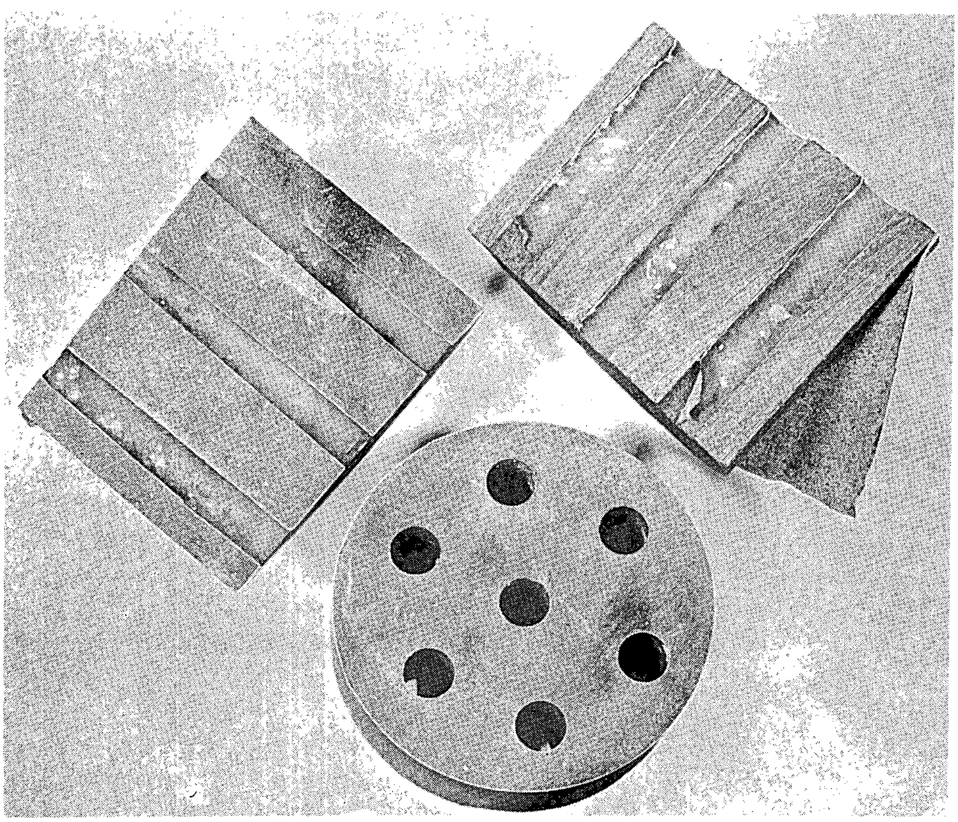


35X RM9654

FIGURE 2. COPPER PLATING ON GRAPHITE CORE



1X RM9653

FIGURE 3. COPPER PLATING ON GRAPHITE CORE SHOWING UNIFORMITY OF COATING

Copper was partially stripped from graphite in upper right section to provide better contrast.

[redacted]

[redacted]

A uniform 0.005-in. coating was obtained both inside the coolant channels and on the outside of the cylinder. Continuity of the copper coating was achieved regardless of the pores inherent in the graphite. A typical copper-graphite interface is shown in Figure 2, while the over-all coating is shown in Figure 3.

Assembly and Evacuation of Cans

The same assembly techniques were used for both Inconel X and Type 316 stainless steel containers.

The graphite was machined into cylinders 2-3/4 in. in diameter by 3-1/4 in. long. Seven 0.375-in.-diameter holes were then drilled, with the use of a template, at the apexes of six equilateral triangles, 0.906 in. on a side, radiating from the center of the cylinder (see Figure 3). The cores that were coated with copper were then electroplated. Using the same template, 0.375-in. holes were drilled in the 0.187-in. header plate that had been machined to 2-3/4 in. in diameter. Coolant-channel cladding tubes were cut to a length that would extend approximately 0.125 in. beyond the header when it was in place (Figure 4). This was done to facilitate welding. Can material was sheared to a width equal to the length of the coolant-channel tubes. The tubes were press fitted into the cylinder and headers were then put into place. The can material was formed around the core and header and clamped tightly in place until welded as shown in Figure 4.

Two methods of welding and closing the cans were used. In the first method the cans were welded in a tank under a helium atmosphere. In this method complete closure of the can was made, entrapping helium inside as well as the air already in the pores of the graphite. When these cans were thermal cycled or heat treated, they deformed by bulging or ruptured as shown in Figure 5 from the increase in internal pressure brought about by the expansion of the entrapped and reaction gases. In some cases the weld ruptured severely as shown in Figure 6 while other cans developed small leaks which prevented the buildup of rupture pressures.

In the second method the welding was done in air and an evacuation tube was welded into a hole drilled in one header. The welded cans were placed under water and pressurized with hydrogen at 30 psi to test for weld integrity. The cans were then placed in a cold furnace and evacuated. The furnace temperature was slowly increased to 1200 F and maintained until a pressure of 5×10^{-3} mm of mercury or less was obtained. The cans were then cooled under vacuum and sealed.

In an attempt to obtain a more intimate contact for heat-transfer purposes between core and cladding than is possible by hand assembly alone, hydrostatic pressing at 1500 F and 10,000 psi, and cold hydrostatic pressing at 39,500 psi were studied. The Inconel X cans ruptured at all welds during the hot hydrostatic pressing. It was believed that a brittle phase was formed in the weld zone (Figure 7). Weld cracks developed in some cans during cold hydrostatic pressing. In others the cans were deformed more in the middle than they were at the ends.

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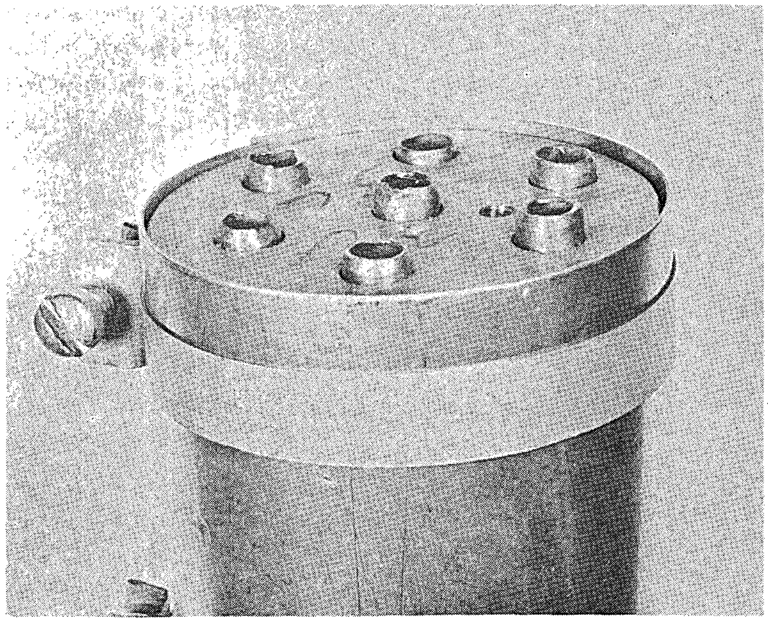
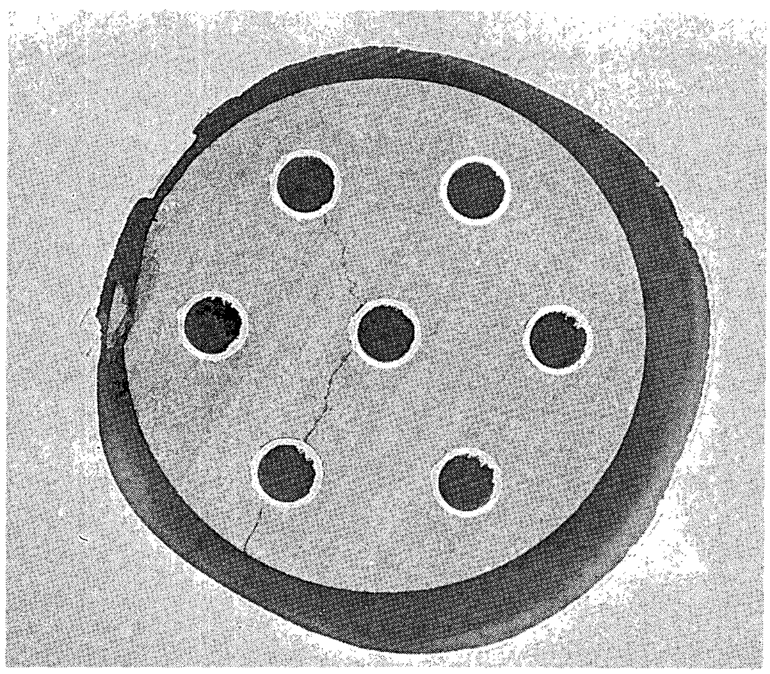


1X RM10442

FIGURE 4. ASSEMBLED CAN BEFORE WELDING



1X RM10441

FIGURE 5. END VIEW OF RUPTURED TYPE 316 STAINLESS STEEL CAN

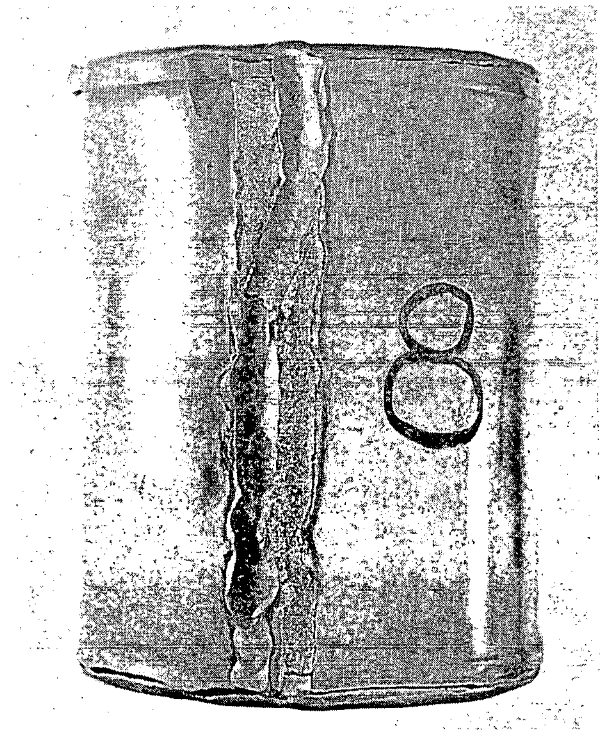
Can had not been evacuated before heat treatment.

[redacted]

1X RM9966

FIGURE 6. STAINLESS STEEL CAN AFTER 107 THERMAL CYCLES BETWEEN 480 AND 1730 F

This can had not been evacuated prior to testing.



1X RM9969

FIGURE 7. INCONEL X CAN AFTER HYDROSTATIC PRESSING FOR 4 HR AT 1500 F WITH A PRESSURE OF 10,000 PSI

[redacted]

HEAT TREATING AND THERMAL CYCLING

Long-time high-temperature heat treating of representative specimens was carried out for 720 hr at 1750 F in an air-atmosphere furnace. These cans were visually checked daily for deformation and large weld cracks. Inspections were executed by opening the furnace door for a short period of time. The cans were not removed and there was little drop in furnace temperature.

Cans were subjected to 150 thermal cycles between 480 and 1730 F. The cans to be evaluated were placed in the apparatus shown in Figure 8. This apparatus moved the cans into and out of the furnaces by means of a motor-driven chain mechanism activated by a two-point controller-recorder. The controller thermocouple for each can was inserted into the center coolant channel to the middle of the can. The furnaces were controlled at a constant 1750 F. Fans were used to increase the cooling rate. It took approximately 20 min to heat a can from 480 to 1730 F and the same time for cooling, or a total time of 100 hr on test.

When it became evident that carburization and oxidation would prevent the use of Type 316 stainless steel as a cladding material, a second series of Inconel X cans was tested by thermal cycling between 500 and 1800 F for 360 hr.

EXAMINATION OF CANS

Visual Inspection

As each can was removed from the test it was sectioned and studied visually. All welds were examined for breaks or oxidation, the coolant channels were examined for oxide growth, and the graphite core was examined for cracks that might have developed from the difference in the coefficient of thermal expansion between the graphite and metal.

A deformation characterized by barreling was observed in all types of cans that had not been evacuated prior to heat treating or thermal cycling. Very little or no deformation was observed in cans that had been evacuated.

Slight oxidation took place on the surface of the Inconel X cans and the coolant channels remained free of any obstructions. No serious oxidation was observed on the surface of the stainless cans; however, coolant channels made from Type 316 stainless steel were almost completely blocked by oxide. It is believed that this oxide growth occurred when the chromium, which imparts oxidation resistance to stainless steel, reacted with the graphite to form intergranular chromium carbide, thereby allowing the iron to oxidize. Apparently the copper barrier was ineffective.

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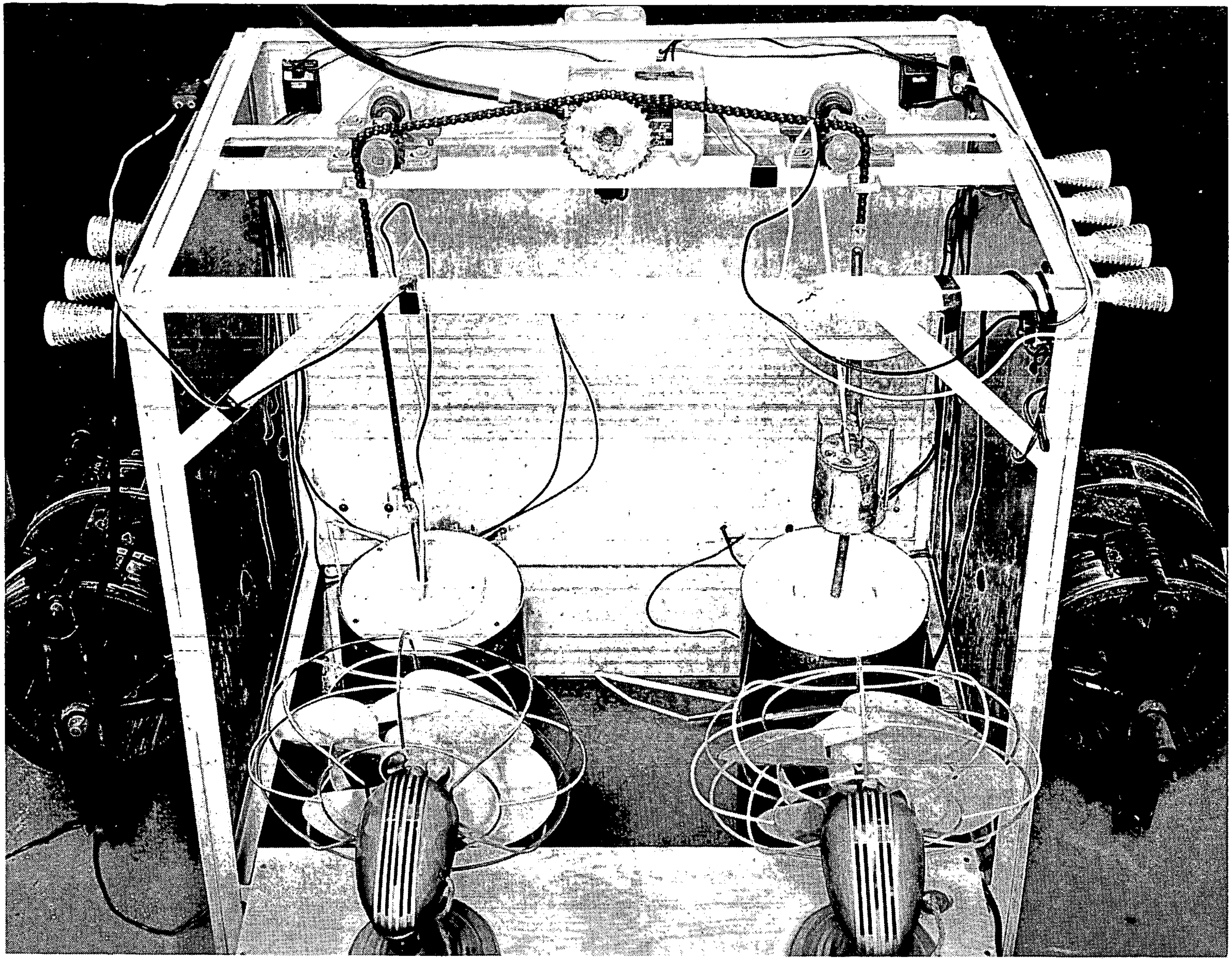


N55263

FIGURE 8. THERMAL-CYCLING APPARATUS

A chemical analysis showed a carbon pickup of 0.04 to 0.05 w/o in Inconel X cans held at 1750 F for 720 hr. Tensile specimens of Inconel X were encased in graphite and held at 1850 F for 500 hr; these exhibited the same carbon pickup as heat-treated cans. When these specimens were subsequently tensile tested at room temperature the results were within 5 per cent of those published for uncarburized Inconel X, 155,000 psi. Figures 9 and 10 are photomicrographs showing a comparison of the carburization in the cladding with the intentionally carburized tensile specimens.

Core cracking was observed in only two cans out of nine that had deformed by barreling and no cores cracked in the cans that had been evacuated before testing.

Bend-test specimens, made from the stock used for tensile testing, successfully withstood 90-deg bends over a 1/8-in. radius.

Welds in Type 316 stainless steel ruptured in a number of cases and oxide formations were observed in others. Inconel X cans developed no weld ruptures in 100-hr tests of heat treating or thermal cycling; however, weld ruptures did occur in cans thermal cycled for 360 hr.

Metallographic Examinations

Photomicrographs were taken of cans that had undergone heat treatment for 720 hr at 1750 F since this produced the most extensive carburization of the cladding materials.

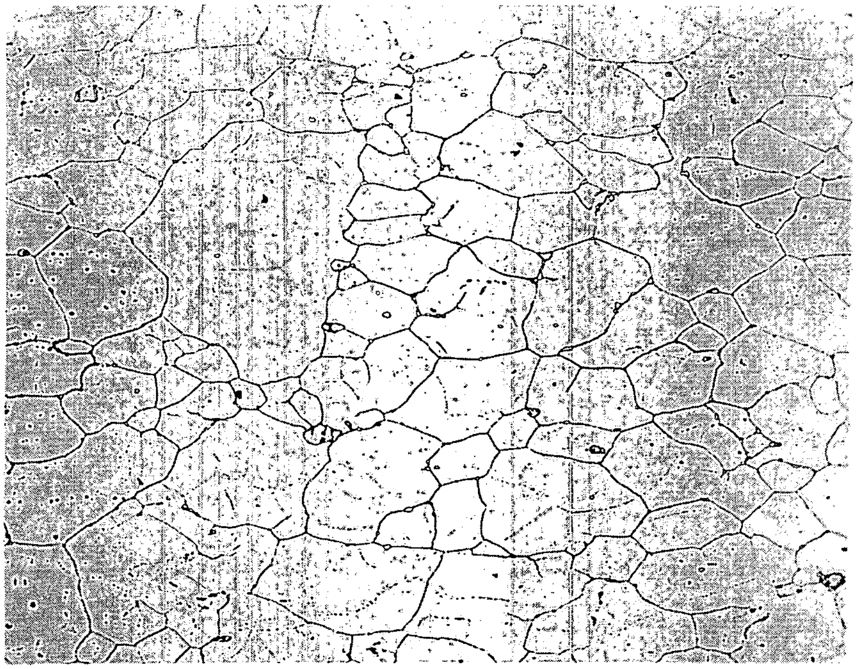
Figure 11 shows the beginning of oxide growth on the surface of the stainless steel. In Figure 12 the growth has nearly consumed the original metal.

Figure 13 shows cracks at both the air-to-metal and graphite-to-metal interfaces; however, the oxidized surface is not deep and the carburization does not greatly affect the strength of Inconel X.

SILICON-COATED GRAPHITE

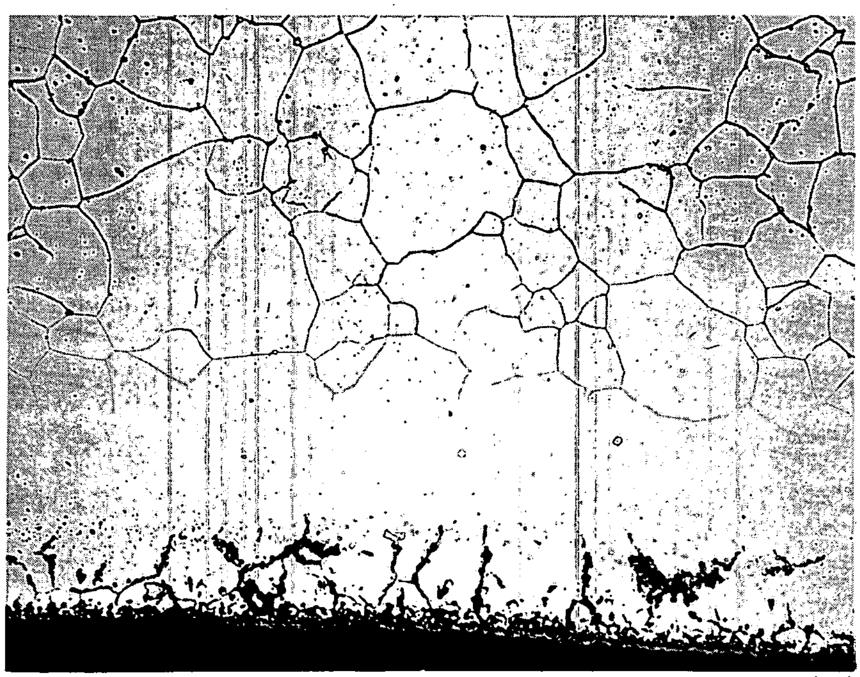
Shortly before expiration of the study a cube of silicon-coated graphite* was obtained. It was hoped that the silicon coating would minimize carburization of the Type 316 stainless steel. The cube was clad with stainless steel and heat treated at 1800 F for 624 hr. The silicon diffused into the stainless steel, forming a diffusion zone of sufficiently high silicon content to facilitate the formation of a secondary phase, as shown in Figure 14; however, there was no carburization and the stainless steel remained ductile.

*Obtained from the Minnesota Mining and Manufacturing Company, Saint Paul, Minnesota.



250X RM10610

FIGURE 9. INCONEL X TENSILE SPECIMEN AFTER 500 HR AT 1850 F BETWEEN GRAPHITE BLOCKS



250 X RM10606

FIGURE 10. INCONEL X CAN HEAT TREATED FOR 720 HR AT 1750 F

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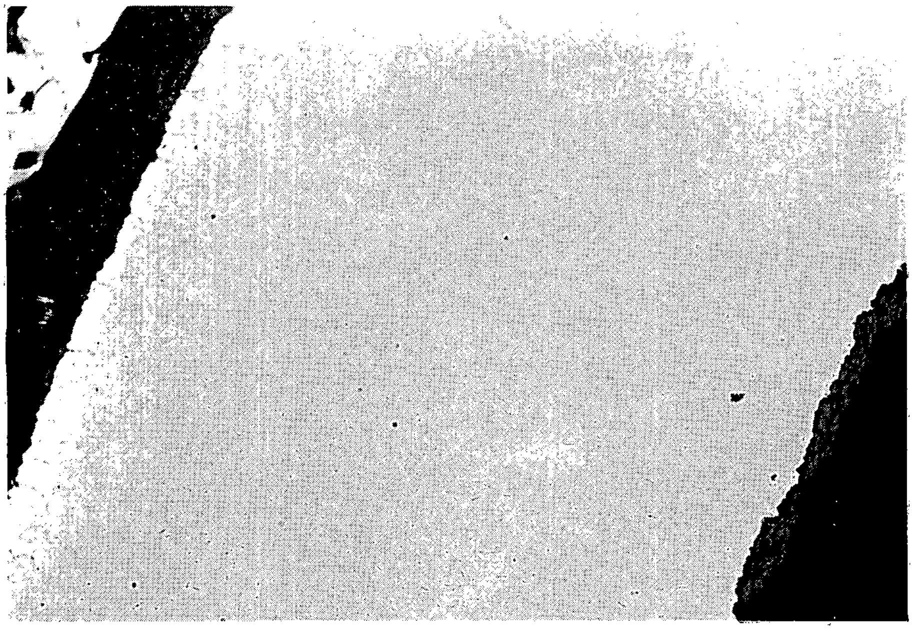

FIGURE 11. BEGINNING OF OXIDE GROWTH IN A STAINLESS STEEL CAN WITH A COPPER-COATED CORE AFTER HEAT TREATMENT AT 1750 F

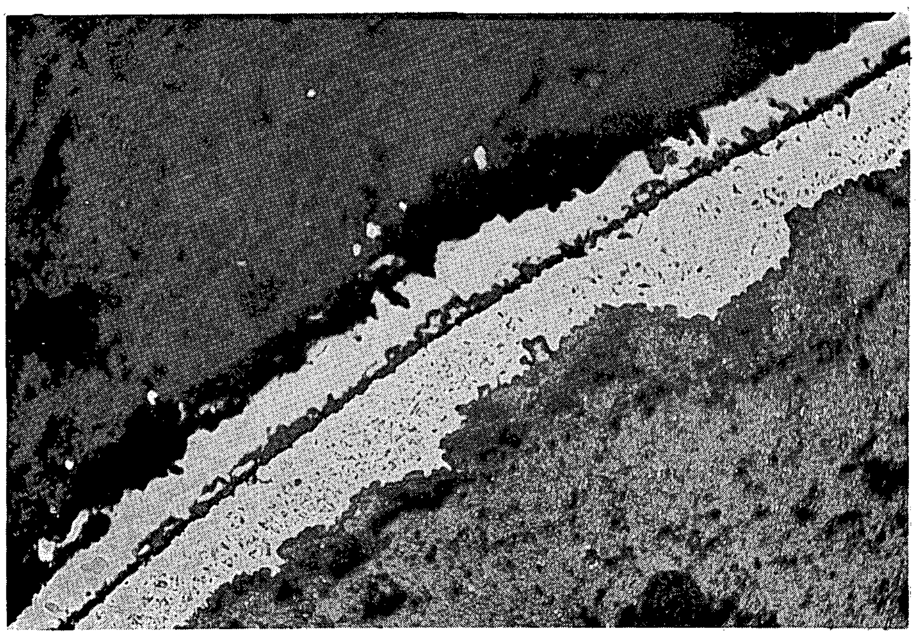

FIGURE 12. NEARLY COMPLETE CARBURIZATION OF THE STAINLESS STEEL IN A CAN WITH A COPPER-COATED CORE AFTER HEAT TREATMENT FOR 720 HR AT 1750 F

[redacted]

[redacted]

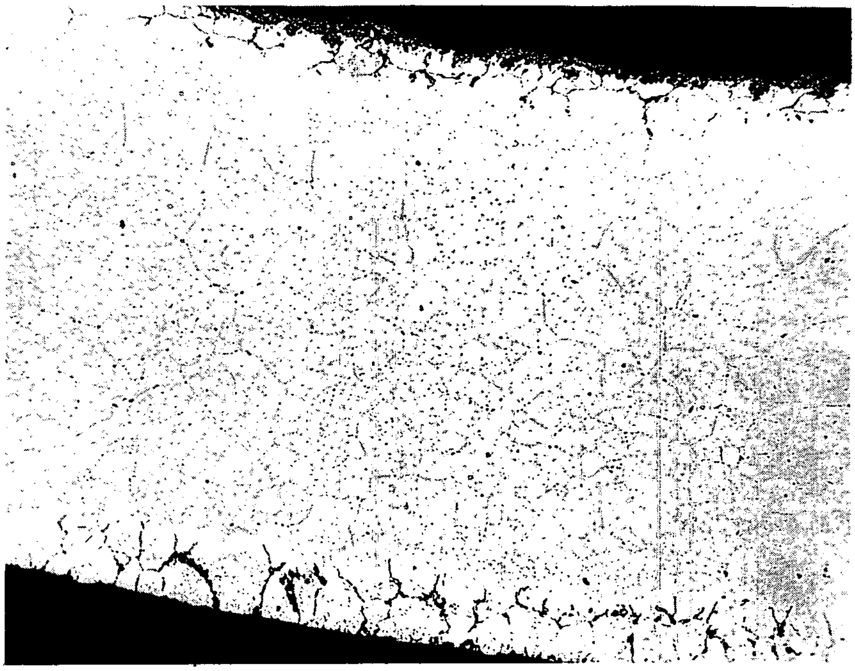

FIGURE 13. INCONEL X AFTER HEAT TREATMENT AT 1750 F FOR 720 HR

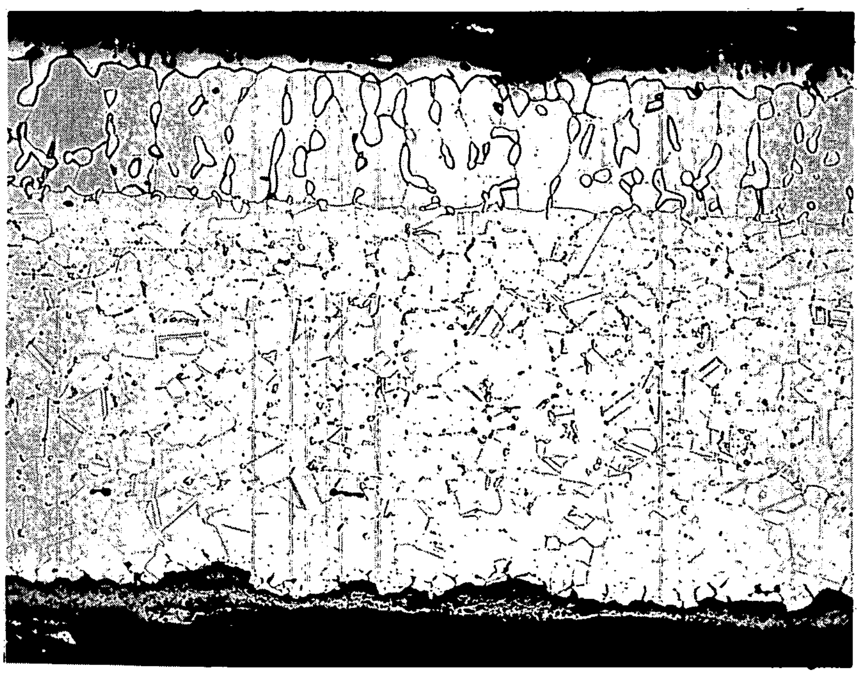

FIGURE 14. TYPE 316 STAINLESS STEEL CLADDING ON SILICON-COATED GRAPHITE AFTER HEAT TREATMENT FOR 624 HR AT 1800 F

[redacted]

[redacted]

SUMMARY

An investigation to develop techniques for canning massive sections of fueled graphite, containing tubular coolant channels, with structural material has been conducted. Nonfueled prototype cylinders, 2-3/4 in. in diameter by 3 in. in length, containing 3/8-in.-diameter coolant channels placed at the apexes of equilateral triangles, were prepared for the investigation.

Cans made from both Inconel X and Type 316 stainless steel were investigated in this study. Copper-coated graphite cores were tested with both types of cans in an attempt to minimize carburization of the metal. Cans of both types of structural material were thermal cycled between 480 and 1730 F and heat treated at 1750 F for 720 hr with and without copper-coated cores.

Barreling occurred in all cans that were sealed without evacuating the entrapped gases. Cans that were evacuated at 1200 F to a pressure of 5 μ or less did not deform during testing.

Cans made from stainless steel, with and without copper-coated cores, developed weld cracks and oxide growths. No weld cracks and very little oxidation occurred in cans made from Inconel X either with or without a copper barrier. However, ruptures appeared in a few Inconel X cans parallel with the side weld of the cans.

Inconel X tensile specimens subjected to a carburizing environment gave a tensile strength, at room temperature, that was within 5 per cent of the strength of uncarburized Inconel X and exhibited good ductility.

Type 316 stainless steel, with or without a copper barrier, oxidizes severely when used as a cladding material for graphite. Inconel X neither oxidizes excessively nor loses its strength when subjected to a carburizing environment under test conditions. Copper coating the graphite core is unnecessary when Inconel X is used as the canning material. Silicon coating on graphite prevents carburization of Type 316 stainless steel during heat treating. While silicon-coated graphite appears to hold great promise, there still remains much research that should be done, such as, thermal cycling and heat treating of clad silicon-coated specimens, and silicon-coated graphite clad with different structural materials.

REFERENCE

(1) Gerds, A. F., and Mallett, M. W., "The Compatibility of a Number of Metals and Alloys with Graphite", BMI-1261 (April 14, 1958).

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