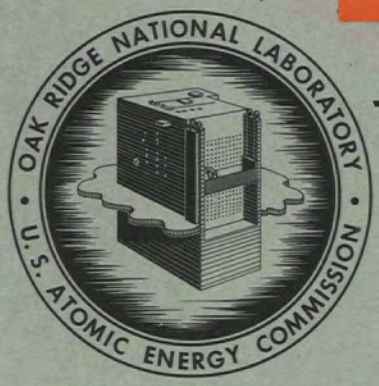
ORNL-2398
UC-25 – Metals, Ceramics, and Materials
TID-4500 (34th ed.)

CARBURIZATION AND CHEMICAL TREATMENTS FOR RECOVERY OF URANIUM FROM STAINLESS STEEL FUEL ELEMENTS

R. E. Adams
E. S. Bomar, Jr.



OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price $3.00. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U.S. Department of Commerce, Springfield, Virginia

ORNL-2398

Contract No. W-7405-eng-26

METALS AND CERAMICS DIVISION

CARBURIZATION AND CHEMICAL TREATMENTS FOR RECOVERY OF URANIUM FROM STAINLESS STEEL FUEL ELEMENTS

R. E. Adams and E. S. Bomar, Jr.

NOVEMBER 1964

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

CONTENTS

FOREWORD

This report is based on experimental work done during 1954–1958, and pertinent information was briefly reported in the various periodic reports issued during that time by the Metallurgy Division. At the conclusion of the work, a summary record report was prepared for limited internal distribution. That report has been revised and is now being issued so that the results of this research will be more generally available.

CARBURIZATION AND CHEMICAL TREATMENTS FOR RECOVERY OF URANIUM FROM STAINLESS STEEL FUEL ELEMENTS

R. E. Adams and E. S. Bomar, Jr.

ABSTRACT

We have investigated metallurgical treatments to simplify reprocessing of spent stainless steel fuel elements. Gas carburization and heat treatments were used to destroy the corrosion resistance of the fuel element material so that simple chemical treatments could expose and dissolve the unburned uranium. Our objective has been to develop specific combinations of metallurgical and chemical techniques that would permit the use of conventional stainless steel equipment for dissolution and subsequent separations. Two promising processes were demonstrated on the plate-type fuel elements developed for the Army Package Power Reactor, in which uranium dioxide is dispersed in a matrix of stainless steel.

In the first process, approximately 2.5% C was introduced into the 0.030-in.-thick dispersion plates by treatment with a stream of 18% CH_4 in dry hydrogen for 4 hr at 950°C or 1 hr at 1050°C. Homogenization for 2 hr at 1100°C distributed the carbon uniformly. Thus treated, the stainless steel dissolved in 4 to 6 hr in boiling 3 M HNO_3, leaving a residue of insoluble chromium-containing carbides. The acid solution from small-scale tests contained up to 99.98% of the uranium. We recovered 99.89% of the uranium in a single test with a full-size APPR fuel element.

In the second process, approximately 0.3% C was introduced by briefer carburization. After homogenization for 2 hr at 1150°C and sensitization for 2 hr at 650°C, the stainless steel matrix was disintegrated by intergranular attack with acidified copper sulfate solution. Approximately 80% of the stainless steel and all of the uranium oxide were left undissolved. We then recovered 99.5% of the uranium by leaching the residue with 10 M HNO_3.

The advantages of these processes are that (1) the chemical solutions used are essentially inert to stainless steel so that conventional dissolvers and piping may be used, (2) the unburned uranium is recovered in nitric acid solutions, which are compatible with existing processes and equipment for uranium purification, and (3) the radioactive waste volumes are decreased because 20 to 80% of the stainless steel is left for storage as chemically inert solids and the uranium is dissolved in a relatively small volume.

INTRODUCTION

The recovery of unburned uranium and the storage of waste products from spent reactor fuel elements are important items in the cost of nuclear reactor operation. The usual method of treatment is chemical dissolution of the fuel element, preferably in nitric acid, and separation of the uranium from the waste products by solvent extraction from nitrate solutions. The liquid waste, containing the radioactive products, must be permanently stored to avoid contamination of the surroundings.

The problems of dissolution of stainless steel fuel elements and storage of waste from them are especially difficult. Because stainless steels are particularly inert to nitric acid, spent stainless steel fuel elements are dissolved in hydrochloric or sulfuric acids. Special materials and techniques are required to handle and store these highly corrosive solutions. In addition, solvent extraction processes are based on nitrate solutions; so further costs are involved in preparation of the uranium-containing solutions for extraction.

We have investigated pretreatment by carburization as a method for destroying the corrosion resistance of spent stainless steel fuel elements. Carbon can readily be added to stainless steel by gas carburization. The carbon combines with the chromium in the steel, and chromium is selectively removed from the matrix phase by precipitation as chromium-rich carbides. Thus depleted in chromium, the metal is no longer able to form the passive films that are responsible for the chemical inertness of the stainless steels. Pretreatment by carburization, therefore, renders stainless steel fuel elements susceptible to dissolution by relatively uncorrosive reagents compatible with stainless steel processing equipment.

We have investigated two essentially different processes that utilize carburization to render stainless steel fuel elements susceptible to chemical attack. In the first, a rather high carbon concentration (from 2 to 3%) is introduced to precipitate the chromium sufficiently completely that the matrix of the fuel plates can be completely dissolved. In the other, a much lower carbon concentration (approximately 0.3%) combined with a sensitizing heat treatment depletes the grain boundaries of dissolved chromium. In this second approach, intergranular chemical attack

disintegrates the stainless steel and exposes the fuel while leaving the bulk of the stainless steel as undissolved granules.

FUEL ELEMENT MATERIAL

The fuel elements to which this work was immediately directed are those used in the APPR (SM-1). These elements (illustrated in Fig. 1) consist of 18 parallel fuel plates brazed into side plates. The fuel-bearing core of each composite fuel plate has been compacted at 33 tsi, sintered at 1200°C in hydrogen, and then clad and fabricated by the picture-frame technique.[1] The finished fuel plates have a 0.005-in.-thick clad. The core, 0.020 in. thick, contains up to 34 vol % UO_2. The side plates contain no uranium and are 0.050 in. thick. The fuel element is about 27 in. long and just under 3 in. square.

Different types of stainless steels have been considered for use in APPR fuel elements. Originally, the clad, the core matrix, and the side plate were all to be made of types 304 or 304ELC stainless steels; these are austenitic steels containing about 19% Cr, 9% Ni, 2% Mn, 0.07 or 0.03% C (respectively), and balance Fe. When production of fuel elements was started, a modified type 302B stainless steel powder was used for the core matrix. The composition of type 302B stainless steel is similar to that given above, except that it also contains 2 to 3% Si. Elements also have been made in which both the clad and the core matrix were of type 347 stainless steel, which contains about 19% Cr and 9% Ni and is stabilized with about 0.8% Nb.

The principles upon which the processes reported here are based apply to several types of stainless steels. Therefore, the processes may be useful for fuel elements made of other types of stainless steels as well as types 304 and 347.

---

[1] J. E. Cunningham et al., Specifications and Fabrication Procedures for APPR-1 Core II Stationary Fuel Elements, ORNL-2649 (Jan. 29, 1959).

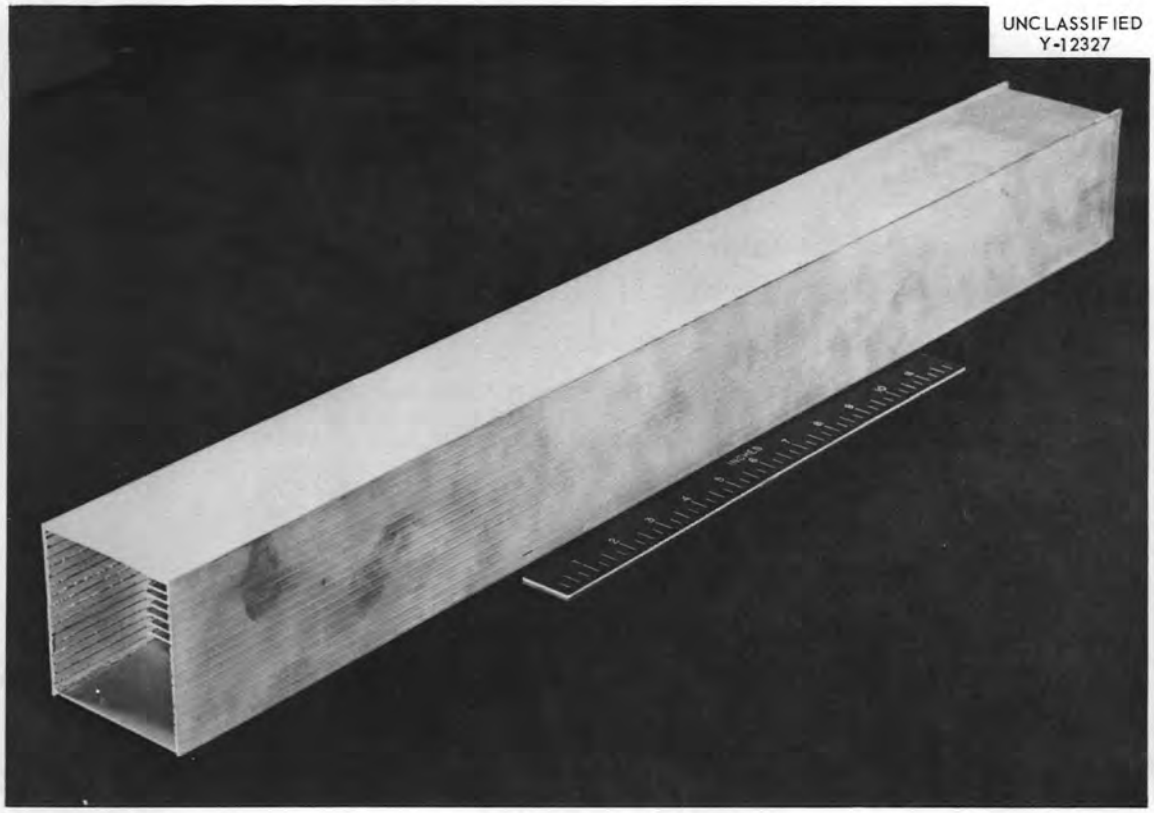


Fig. 1. Fuel Element for APPR.

PROCESS STEPS

Research on carburization as a method of facilitating recovery of uranium from spent stainless steel fuel elements was divided into metallurgical and chemical research. Metallurgical research was concerned with the destruction of passivity of the fuel element material. Chemical research was concerned with exposing, dissolving, and recovering the unburned uranium from the carburized fuel element.

The degree to which passivity of stainless steel can be destroyed with carbon is controlled by the amount of carbon added, by its distribution in the fuel element, and by the way in which carbon and chromium combine to precipitate as chromium-rich carbides. The metallurgical treatments may be regarded as three separate processes:

1. carburization, the addition of carbon to the fuel element,
2. homogenization, the distribution of the carbon uniformly through the thickness of the fuel element material, and
3. sensitization, the precipitation of the chromium-rich carbides from the austenitic solid solution.

A discussion of the variables of these metallurgical processes as they apply to this investigation appears below. Appendix A gives a more detailed discussion of the behavior of carbon in stainless steel. Similarly, Appendix B discusses the factors governing intergranular attack.

The chemical treatments may also be considered as separate processes:

1. fuel element dissolution, the process in which the chromium-depleted portions of the stainless steel are dissolved,
2. uranium dissolution, the leaching of the uranium from the insoluble portions of the fuel element material, and
3. uranium recovery, the recovery and separation of the uranium from the waste products.

Carburization

Gas carburization is a well-developed commercial process for adding carbon to low-alloy steel to improve its surface hardness. In gas carburization, the metal is heated in a circulating atmosphere containing gaseous carbon compounds, which can react to add carbon to the metal surface. Immediately upon formation, this carbon starts to dissolve in the metal and diffuses to the interior. The composition of the carburizing atmosphere and the carburizing temperature control the chemical reactions between the metal and the gas and determine the carbon concentration at the surface of the metal. The surface quickly reaches equilibrium with any specific carburizing atmosphere, and additional carbon reacts at the surface only to replace the carbon that diffuses inward.

The steel absorbs carbon very rapidly early in the carburizing cycle but more slowly as carburization proceeds. The rate of carburization depends on the composition of the gas in contact with the metal, the carburizing temperature, the thickness of the material being carburized, and the chemical composition of the metal. The total quantity of carbon added

depends, in addition, on the length of time the element is exposed to the carburizing atmosphere. The composition of the carburizing gas is not constant along the length of the fuel element. As the carburizing atmosphere flows over the metal, it loses carbon to the metal and its caburizing power is reduced. This results in a tendency for the metal nearest the gas inlet to be carburized most rapidly and the carbon content in the metal to decrease along the direction of gas flow. The extent to which this effect can be minimized to produce uniform carburization depends on the geometry of the metal, the carburizing temperature, its gradient along the length of the fuel element, and the flow rate, the degree of mixing, and the composition of the carburizing atmosphere.

Homogenization

A carburized steel has a maximum carbon content at the outside surface and a smaller carbon content at the center. In order that uranium at the center of the fuel plates may be released by the chemical dissolution, sufficient carbon must reach the center of the fuel plates. Homogenizing treatments have been used after carburization to cause the carbon to diffuse uniformly through the thickness of carburized fuel plates. The homogenizing treatment is simply a diffusion treatment and is time and temperature dependent. Satisfactory results have been obtained by heating at 1100°C for 2 hr, and some results indicate that a shorter time may be sufficient. An inert atmosphere is necessary to avoid changing the carbon concentration near the surface and thus affecting the behavior during dissolution. The uniform carbon distribution obtained by the homogenizing treatment will be demonstrated in photomicrographs in later portions of this report.

Sensitization

The manner in which carbon and chromium are combined in the fuel plates is affected by the rate of cooling from high temperatures and by subsequent heat treatments at lower temperatures. For instance, carbon may be retained in solid solution in rapidly cooled alloys. At temperatures between 450 and 800°C, the carbon migrates to the grain boundaries

and precipitates as chromium carbide. Such treatments make stainless steels corrode selectively at their grain boundaries and have been termed "sensitizing" treatments. Sensitizing treatments are an important part of the recovery process based on intergranular corrosion. Optimum times and temperatures for sensitization have not been established, but with steels containing approximately 0.2 to 0.4% C, a 2-hr treatment at 650°C is adequate.

Sensitizing treatments are not necessary when the steel contains a high concentration of carbon and complete dissolution of the matrix phase is sought. However, the dissolution behavior might be improved by such treatments.

PROCESS BASED ON EXTENSIVE CARBURIZATION

The major part of this research was concerned with the addition of enough carbon to the fuel element material that nearly complete dissolution of the matrix phase could be obtained. Small specimens of solid stainless steel and pieces cut from APPR fuel plates were tested first. Finally, we studied carburization and uranium recovery on full-size APPR fuel elements.

Experimental Work

Carburization of Small Test Specimens

The carburization of stainless steels was investigated with specimens sheared from sheet stock. We used small specimens of solid (i.e., unfueled) type 304 stainless steel 0.031 × 1.5 × 0.5 in. to investigate carburizing variables and to test chemical activity. Specimens for uranium-recovery tests were sheared from dummy APPR fuel plates and were 3 × 1 × 0.031 in. Edges where the core was exposed by shearing were sometimes coated with a brazing alloy that resisted carburization and chemical attack. Before they were carburized, all specimens were annealed in dry hydrogen at 1150°C to produce a metallurgical structure simulating that obtained when a fuel element is brazed. Specimens were cleaned in acetone just before carburization.

The degree of carburization was determined by measuring the weight gain of the specimens. As a check, two carburized specimens were analyzed, and the results agreed closely with those calculated from weight gain:

Specimen Number	Carbon by Weight Gain (%)	Analyzed Carbon Content (%)
46B	1.58	1.58
58B	2.76	2.81

Carburization was tested in an electrically heated ceramic tube furnace (Burrell Globar Furnace B-19-T) with a tube 2.3 in. in diameter and 48 in. long. The carburizing atmospheres were made by mixing natural gas (97% CH_4) with a diluting gas in a single 0.25-in.-diam tube about 1 ft from the furnace chamber. The rate of flow of each gas was measured with an orifice-type flow meter, and compositions and flow rates were based on volumes at room temperature and pressure. The spent gas was burned as it issued from an 0.06-in.-diam tube at the end of the furnace. Usually, two to four specimens, which were held on edge parallel to the gas flow by a wire frame in a carburized stainless steel basket, were carburized together. Specimens were pushed into the hot furnace in the diluting gas. At the time estimated that the specimens reached furnace temperature, methane was added to the gas stream. After treatment for the desired time, the methane flow was stopped and the specimens were pulled to the cold end of the furnace.

Early tests were made with atmospheres of about 30% CH_4–70% tank nitrogen flowing at approximately 0.8 fpm. The steel was carburized but the surface was slightly oxidized and the carburization was uneven. Considerable soot developed in the gas but it did not deposit on the specimens.

Dry hydrogen was a much more satisfactory diluting gas. The specimens remained clean and bright, and no evidence of soot was found. The tank hydrogen was purified by passage through a Deoxo unit and a Pittsburgh Lectrodryer, which dried it to a dew point of about −40 to −51°C, as measured by an Alnor Dew Pointer. Consistently good results were obtained with 18% CH_4–82% dry H_2 flowing over the specimens at approximately 1.5 fpm.

Figure 2 shows the carbon content achieved in small 0.031-in.-thick specimens of type 304 stainless steel as a function of carburizing time and

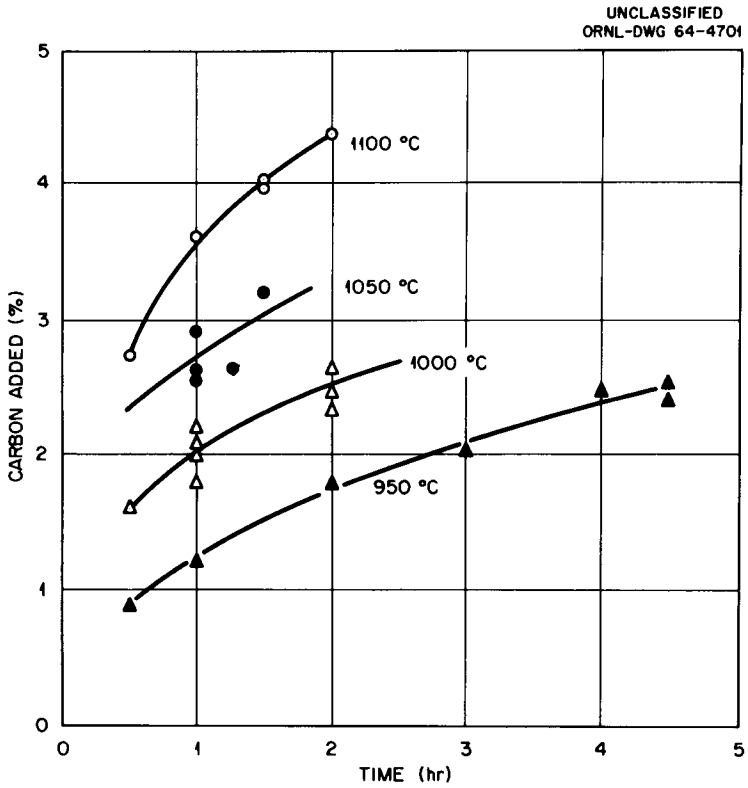


Fig. 2. Results of Carburizing 0.031-in.-thick Type 304 Stainless Steel with 18% CH_4–82% H_2.

temperature. Since the rate of carburization is expressed in terms of percent carbon in the steel, the values are valid only for specimens of the thickness shown.

To extend the application of this work to other fuel elements, we have calculated carburization rates and carbon concentrations for other plate thicknesses. Figure 3 shows the time required to add 2.5% C to plates of different thicknesses in the temperature range of 950 to 1050°C. Figure 4 shows the time required at 950°C to add different carbon contents to plates of various thicknesses.

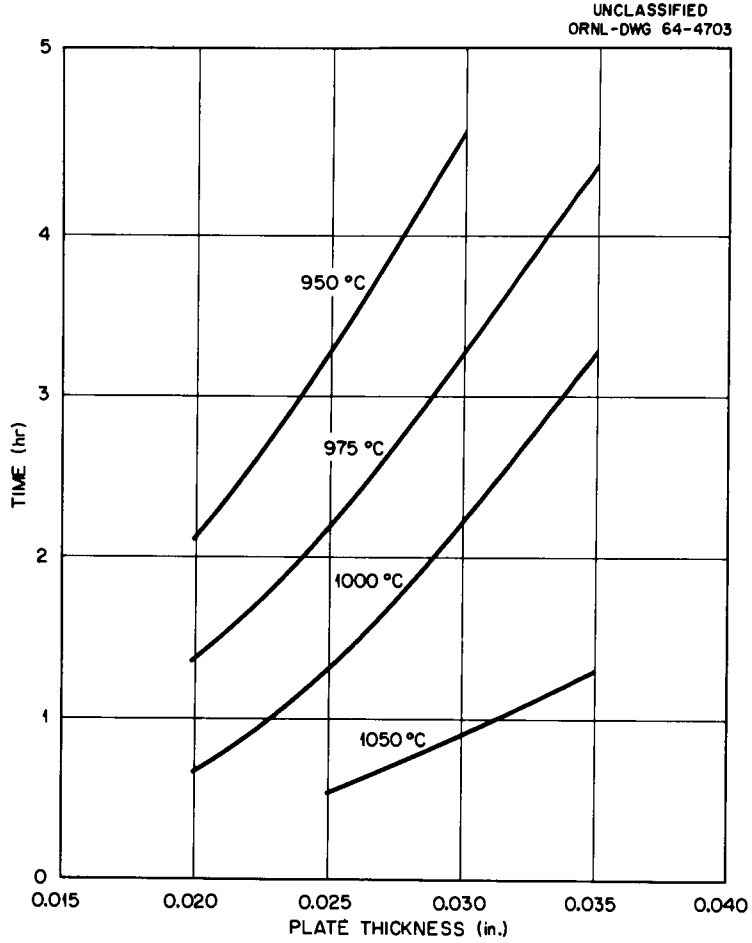


Fig. 3. Time Required to Add 2.5% C to Type 304 Stainless Steel Plates of Different Thickness. (Based on carburization from both sides; for carburization from only one side, use values for plate twice as thick.) Gas mixture composed of 18% CH_4 and 82% H_2.

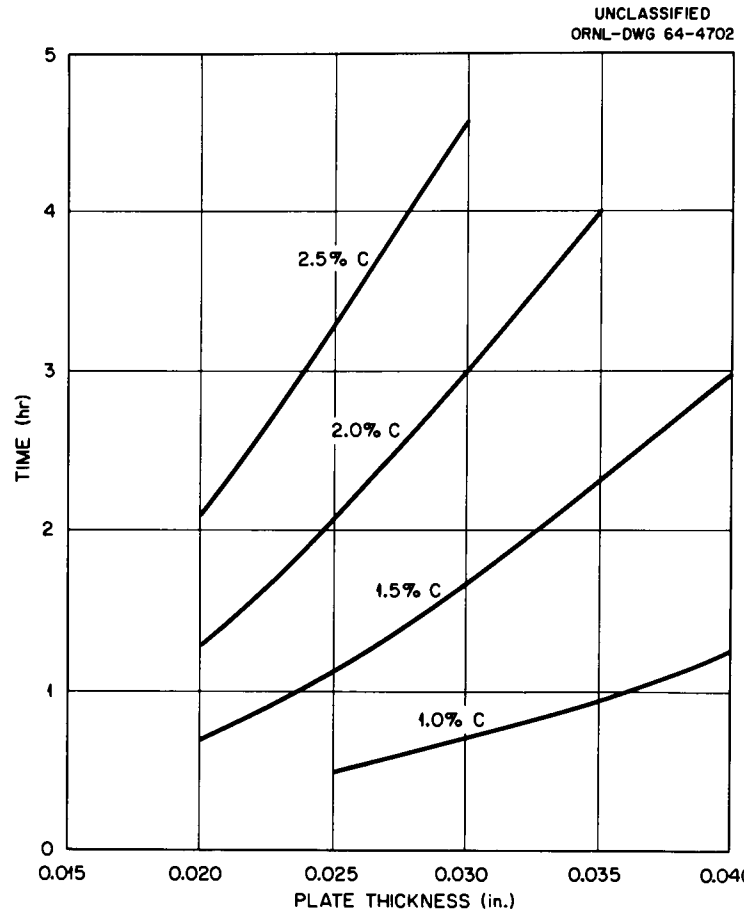


Fig. 4 Time Required at 950°C to Add Different Contents of Carbon to Type 304 Stainless Steel Plates of Various Thicknesses. (Based on carburization from both sides.) Gas mixture composed of 18% CH_4 and 82% H_2.

We also tested the effects of other carburizing atmospheres, flow rates, and diluents. Table 1 presents a selection of the results. The more significant observations follow:

1. Types 304 and 347 stainless steels and similar APPR fuel materials were readily carburized at temperatures from 925 to 1100°C in an atmosphere of 18% CH_4 in dry hydrogen flowing at about 1.5 fpm. The results did not critically depend on methane concentration or flow rate.

2. Atmospheres consisting of methane and nitrogen or helium could be used to carburize stainless steel, but excess methane decomposed to form soot. Methane pyrolysis increased with increasing temperature and methane-hydrogen ratio.

3. Carburizing atmospheres of methane and hydrogen could be considerably diluted with dry helium or nitrogen without sooting, tarnishing, or decreasing the carburization rate.

4. On prolonged heating in hydrogen-methane mixtures, type 304 stainless steel carburized until it became saturated with about 5.7% C at a temperature of 1060°C or > 4.9% C at 960°C.

Carburization of APPR Fuel Elements

Full-size APPR fuel elements were carburized to ascertain whether their geometry would limit the application of the method. Because of its large metal area and small volume for gas flow between the fuel plates, a complete element extracts considerable carbon from the gas as it flows to the exhaust end of the fuel element. Thus the carbon concentrations at the inlet and at the exhaust end of the fuel element tend to be unequal. This effect can be minimized by using high rates of gas flow, atmospheres rich in methane, and low carburizing temperatures.

The APPR fuel elements were carburized in a gas-tight box in a muffle furnace. The carburizing gas entered at one end of the box, passed through the fuel element, and burned as it exhausted through a tube at the other end of the box. Hydrogen was purified by passing through a Deoxo unit and a Lectrodryer. The hydrogen was then mixed with bottled methane to form the carburizing atmosphere. Details of the experimental method are given in Appendix C.

Table 1. Results of Typical Carburizing Tests in Laboratory Furnace; Types 304 or 347 Stainless Steel or Fuel Plate Specimens 0.030-in. Thick

Test Number	Carburizing Temperature (°C)	Time (hr)	Gas Flow Rate[a] (cm^3/min) H_2	CH_4	He	Carbon Content[b] (%)
50	925	2.0	720	170		1.46
51	925	0.75	720	170		0.94
54	950	0.5	740	170		0.88
55	955	1.0	750	170		1.52
86	950	3.0	760	170		2.05
152	950	1.0	760	170		1.20
153	950	4.0	760	170		2.46
161	950	4.5	760	170		2.40
163	950	4.5	760	170		2.55
166	950	2.0	760	170		1.79
47	1000	1.0	750	170		2.06
52	1000	0.5	720	170		1.60
53	1000	2.0	720	170		2.63
80	1000	1.0	760	170		2.20
142	1000	1.0	760	170		2.03
145	1000	2.0	760	170		2.32
154	1000	1.0	760	170		1.80
155	1000	2.0	760	170		2.53
162	1000	2.0	760	170		2.45
164	1000	2.0	760	170		2.50
48	1000	0.5		170	520	1.52
49	1000	1.0		170	720	2.06
43	1050	1.0	750	170		2.90
56	1050	1.0	750	170		2.55
57	1050	1.0	750	170		2.62
68	1050	1.5	750	170		3.20
87	1050	1.0	760	170		2.90
88	1050	1.0	760	170		2.95
159	1050	1.25	760	170		2.63
45	1050	1.0	750	170		2.50
46	1050	1.0	750	60		1.60
68	1050	1.5	750	170		3.20
69	1050	1.0	750	170		2.55
70	1050	1.2	370	80		2.30
71	1050	1.0	180	45		1.50
72	1050	1.0	180	45	690	1.70
73	1050	2.0	180	45	690	3.60
74	1050	1.0	180	45	690	2.70
76	1050	1.0	190	45	690	2.60
77	1050	1.0	190	45		2.10
78	1050	1.0	190	45		1.94
79	1050	1.0	760	170		2.64
81	1050	1.0	500	300		3.07
44	1100	1.0	750	170		3.61
58	1100	0.5	750	170		2.75
67	1100	1.5	750	170		4.01
143	1100	1.5	760	170		3.97
167	1100	2.0	760	170		4.39

[a] Based on volume at ambient temperature and pressure.
[b] Based on weight gain.

The extent of carburization was determined by weight gain. Carbon contents at the inlet and exhaust ends of the fuel element were estimated from the weight gain of small, individually weighed stainless steel specimens hung in the gas stream. The weight gain of the entire fuel element was also determined. Since the fuel plates and side plates had different thicknesses, the average carbon content of the fuel plates was calculated by assuming that the total amount of carbon added was distributed uniformly over the area of both sides of the fuel plates and the side plates. This assumption is slightly in error, since the inside surfaces of the side plates are partially protected by the edges of the fuel plates and the braze.

The pertinent experimental conditions and results are summarized in Table 2. In tests Nos. 3 and 4, methane concentrations of about 15 to 19 vol % at flow rates near 20 fpm resulted in approximately uniform carbon concentrations along the length of the fuel plates. These data are complicated by temperature variations of about 25°C along the fuel element during carburization. The temperature also varied a similar amount with time, especially near the inlet end.

The fuel element carburized in test No. 4 was homogenized for 2 hr at 1100°C, and metallographic specimens were cut from a section 6 in. from the exhaust end of the fuel element. Figures 5 and 6 show that uniform carburization was attained well beyond the edges of the fuel-bearing core, and Fig. 7 shows that the carbon penetrated completely to the center of the core material. Chemical analyses for carbon content were made for several locations in the fuel element carburized in test No. 4. The results are shown in Table 3.

We may conclude from these tests on APPR fuel elements that the geometry of the fuel element does not interfere with the use of richly carburizing atmospheres and that gas flow rates required to add desired amounts of carbon uniformly to the fuel plates are easily obtained.

Dissolution and Uranium Recovery

Once the chromium in stainless steel has been combined with carbon, the steel has little resistance to chemical attack. Savolainen[2] has

[2]J. E. Savolainen, Recovery of Uranium from Spent Stainless Steel Fuel Elements of the Package Reactor, ORNL CF-54-4-39 (April 6, 1954).

Table 2. Results of Carburizing Tests on Full-Size APPR Fuel Elements

Test Number	Carburizing Time (hr)	Total[a] Gas Flow (cfh)	Velocity of Gas Mixture[b] (fpm)	Methane Content[b] (vol %)	Average Temperature (°C) Inlet	Center	Exhaust	Average Carbon Content (%) Inlet Specimen Insert[c]	Fuel Plates[d]	Outlet Specimen Insert[c]
1	4	48	11.5	12.5	918	e	948	1.91	1.29	0.59
2	4	119	28.5	11.8	920	956	952	1.74	2.00	1.48
4	4	74	17.7	19.2	940	965	945	2.59	2.34	2.29
3A	3.5	97	23.3	15.3	e	960	965	1.53	1.83	1.78
3B	3	59	14.1	16.5	937	954	954	1.10	1.10	1.18
Total 3A and 3B	6.5							2.63	2.93	2.95
				Average 3A and 3B		958	960			

[a] Based on volume at ambient temperature and pressure.
[b] Based on flow rates of individual gases.
[c] Based on weight gain of small specimens located at inlet and exhaust end of fuel element.
[d] Based on total carbon added to the fuel element, assuming carbon added uniformly per unit area, and based on uniform plate thickness.
[e] Not recorded because of thermocouple failure.

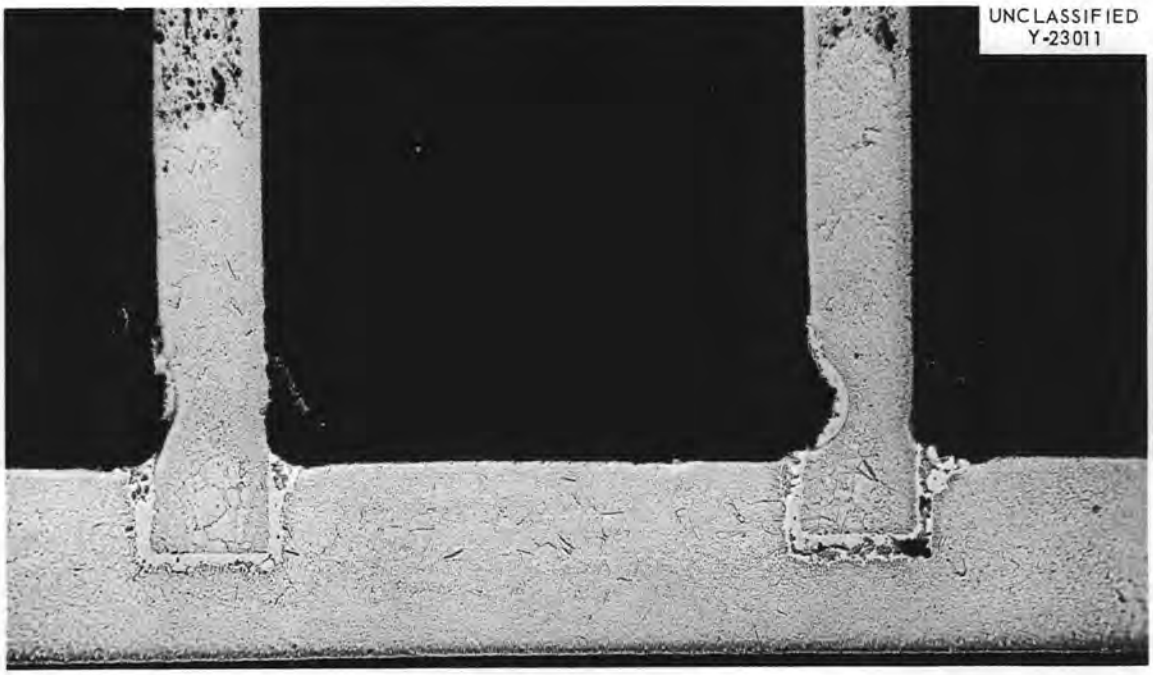


Fig. 5. Microstructure of Carburized and Homogenized APPR Fuel Element. Section was taken 6 in. from exhaust end of the fuel element and shows one side plate and edges of the second and third fuel plates from the top of the element. 20×.

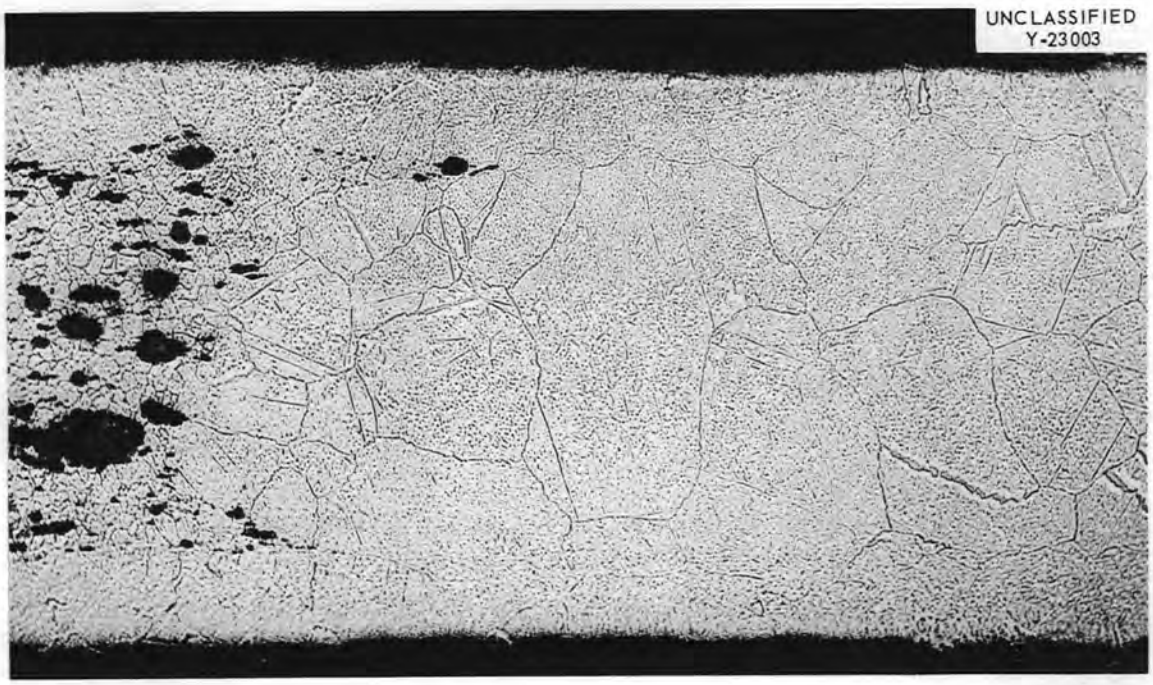


Fig. 6. Microstructure of Edge of Fuel in Third Plate from Top of Specimen Shown in Fig. 5. Analyzed carbon content, 2.17%. 100×.

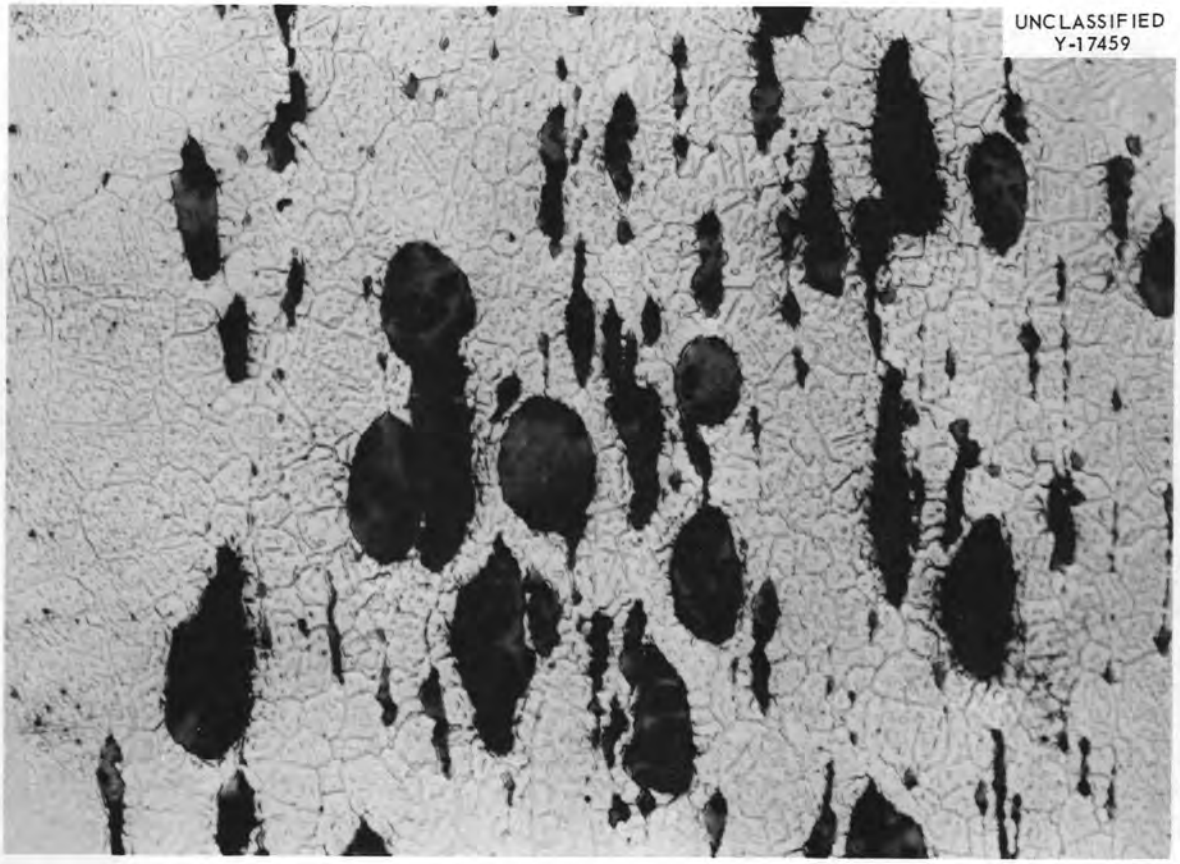


Fig. 7. Microstructure of Core of Carburized and Homogenized APPR Fuel Element. Section was taken 6 in. from exhaust end, near right edge of the 16th fuel plate from the top of the element. Center line of core is 2.7 in. from the left in the photomicrograph. Analyzed carbon content, 2.02%. 250X.

described dissolution of the matrix phase of carburized stainless steel in acidified copper sulfate. Although this method showed promising results in early tests, the use of dilute nitric acid appeared more attractive, and later work has been largely concerned with nitric acid dissolution.

In early experiments, carburized stainless steel dissolved rapidly in approximately 2 M HNO_3, but the reaction ceased after varying amounts of metal had been dissolved. Further work by the Chemical Technology Division showed that the reaction products (presumably nitrogen oxides) caused passivation and that this passivation could be prevented by addition of urea to the solution to destroy the intermediate nitrous acid.

Table 3. Distribution of Carbon in APPR Fuel Element Carburized in Test No. 4

Location	Carbon by Weight Gain[a] (%)	Carbon by Chemical Analyses (%)
Inlet end		
Top plate at end	[c]	2.48[b]
Specimen 0.5 in. from left side	2.58	[c]
Specimen at center	2.59	[c]
Specimen 0.5 in. from right side	2.61	[c]
Bottom plate at end	[c]	2.58[b]
Average inlet end	2.59	2.53
Fuel plates – 21 in. from inlet end		
3rd plate from top – 0.75 in. from right side	[c]	2.17[d]
4th plate from top – 0.75 in. from right side	[c]	2.17[d]
16th plate from top – 0.75 in. from right side	[c]	2.05[d]
16th plate from top – 0.75 in. from left side	[c]	2.02[d]
Exhaust end		
Top plate	[c]	2.46[b]
Specimen 0.5 in. from left side	2.30	[c]
Specimen at center	2.24	[c]
Specimen 0.5 in. from right side	2.34	[c]
Bottom plate	[c]	2.18[b]
Average exhaust end	2.29	2.32

[a] Determined by weight gain of specimens hung in gas stream.
[b] Determined by analysis of top and bottom fuel plate, 0.5 in. from each end.
[c] Not measured.
[d] Specimens analyzed contained about 10 wt % UO_2.

Experiments on small specimens[3] showed the rate of dissolution of carburized stainless steel to be at a maximum at approximately 55°C in 3.0 M HNO_3. Under such conditions, the matrix phase of 0.030-in.-thick stainless steel containing about 2.5% C was completely dissolved in from 2 to 6 hr. The carbides did not dissolve but remained as a porous, friable network that readily collapsed into a fine powder. The weight of the undissolved carbides amounted to approximately 10 times the weight of the carbon.

Small specimens of carburized fuel element material were also treated to study the behavior of the uranium.[2,3] Most of the uranium was recovered in dilute nitric acid solutions, and essentially all of the uranium (99.98% in some tests) was recovered by an additional leaching treatment of 1 hr in boiling 10 M HNO_3.

Since under certain conditions the combination of urea and nitric acid can constitute an explosion hazard, we sought methods of controlling passivation other than urea addition. Evans,[4,5] who has discussed the action of nitric acid on metals, suggests that stirring or bubbling air through the solution may also remove nitrous acid and prevent the reactions believed responsible for passivation. We have demonstrated the use of air to control passivation along with the recovery of uranium from carburized type 347 stainless steel APPR fuel material. In one experiment, a specimen carburized to contain 2.46% C and homogenized at 1100°C for 2 hr was treated for 5.7 hr with 3 M HNO_3 at 50–70°C. Air was bubbled continuously through the solution at a slow rate. No evidence of passivation was found, and the residual solids, after subsequently being leached for 1 hr with boiling 10 M HNO_3, retained only 0.014% of the uranium from the original sample.

---

[3]Experiments by J. E. Savolainen, Chemical Technology Division.

[4]U. R. Evans, Metallic Corrosion, Passivity, and Protection, 2nd ed., Arnold and Co., London, 1946.

[5]U. R. Evans, Trans. Faraday Soc. 40, 120 (1944).

The dissolution of full-size APPR fuel elements has been tested[6] on the elements carburized in tests 3B and 4, Table 2. Approximately one-half of element 3B was treated for 23 hr in 50 liters of a 2.87 M HNO_3 and 0.3 M urea solution. Analysis of samples of the solution showed that the reaction had essentially stopped after approximately 3 hr. In this experiment, the fuel element rested with the fuel plates parallel to the bottom of the dissolver. Both ends of the specimen reacted completely, but the center section did not. We believe that the center of the element was passivated because poor circulation of the solution through the fuel element impaired escape of the the nitrogen oxides.

The center section of the fuel element carburized in test No. 4 was dissolved under conditions similar to those used in the previous test, except that the specimen was slanted to promote convection and the solution was agitated by air sparging. The progress of dissolution is shown in Fig. 8, a plot of analyses of solution samples that had been removed at intervals during dissolution. The reaction was complete in approximately 4.5 hr, although the acid concentration had dropped to about 1 M during the first 2 hr. The matrix phase of the fuel plates reacted completely, and the insoluble carbide network collapsed when the fuel element was removed from the dissolver. Most of the uranium also dissolved, but a leach with boiling 10 M HNO_3 was used to dissolve the uranium completely. The progress of the leaching treatment is shown in Fig. 9. Virtually all of the uranium was dissolved during the first hour.

---

[6]Experiments by J. H. Goode, Chemical Technology Division.

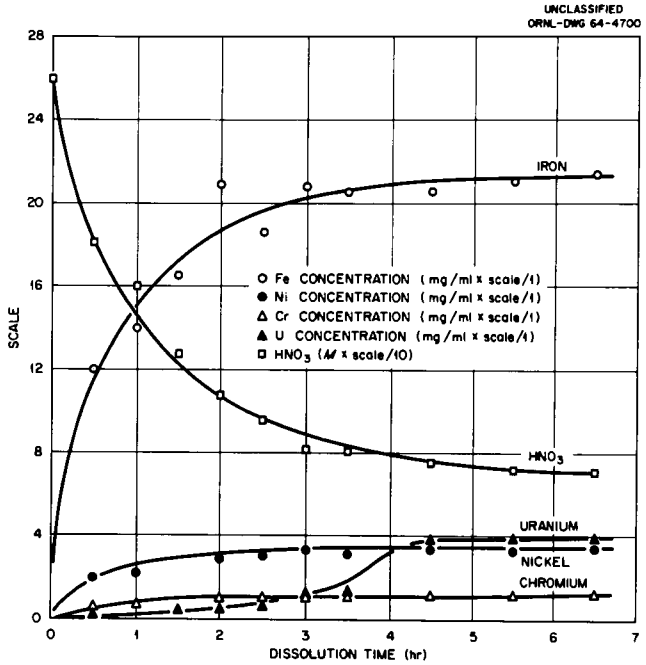


Fig. 8. Dissolution of Carburized APPR Fuel Element in 2.61 M HNO_3 and 0.3 M Urea at 45 to 55°C.

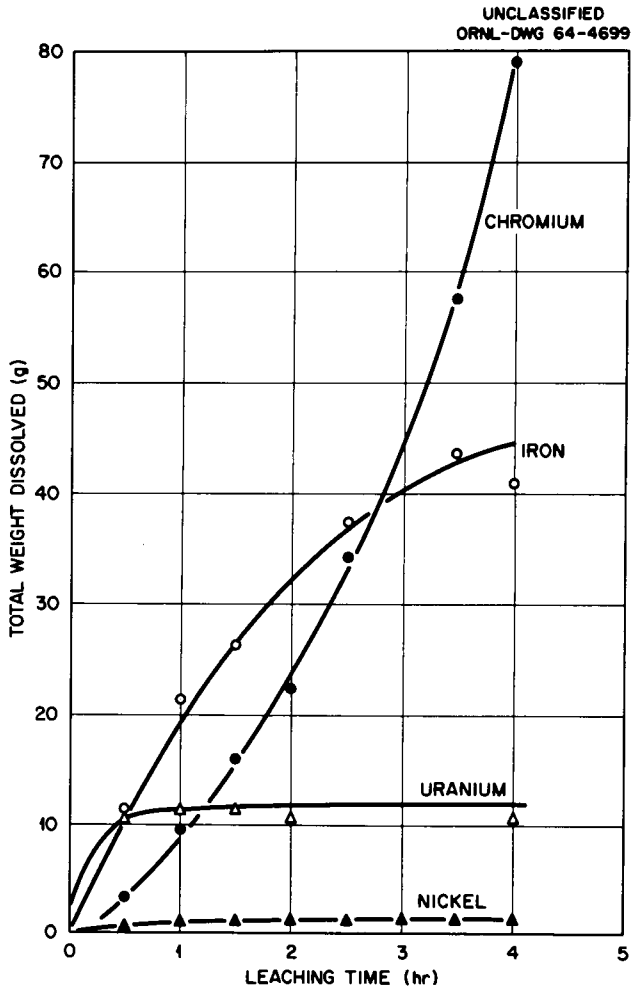


Fig. 9. Analyses of Solution Obtained by Leaching in Boiling 10 M HNO_3 the Residue (800 g) from Dissolving a Carburized APPR Fuel Element in Nitric Acid with Urea (3 liters of solution).

Since the side plates were thicker than the fuel plates, they did not react completely and were removed from the dissolver after the first dissolution treatment. The side plates in Fig. 10 show the uniformity and completeness of the fuel-plate reaction.

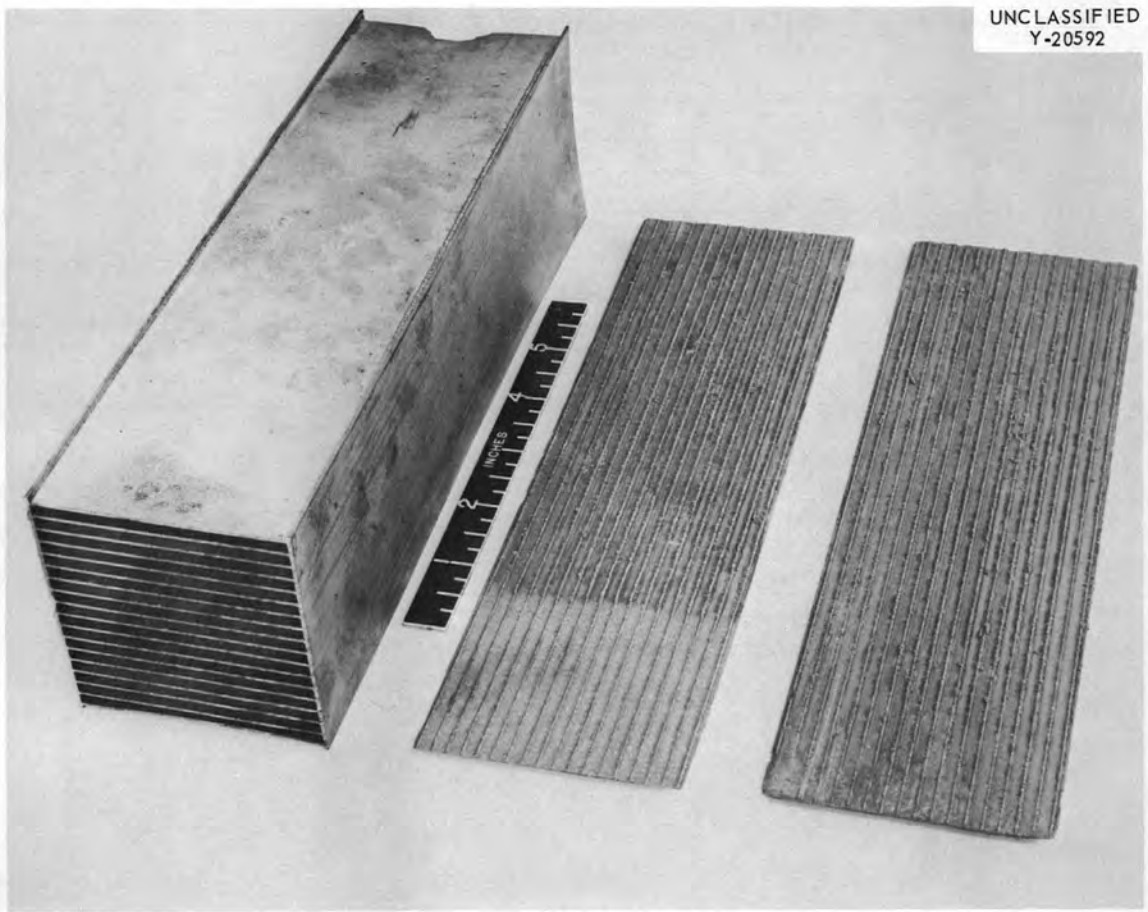


Fig. 10. Left: Carburized and Homogenized Section (Inlet End) of Fuel Element No. 4. Contains about 2.2% C. Right: Side plates from center section of same fuel element after dissolution treatment. Note that all fuel plates were attacked uniformly up to the inside surfaces of the side plates. The near end of one side plate was scrubbed with a fiber brush to indicate the ease of removal of the carbide particles.

The results of the dissolution and leaching treatments are summarized in Table 4. The uranium in the solids (0.11% of the total uranium recovered) represents a loss that might be reduced with improved techniques. Approximately 29% of the stainless steel was left in solid form; the remainder was dissolved in the two nitric acid solutions.

Table 4. Results of Dissolution and Leaching Tests on a Carburized APPR Fuel Element[a]

Source of Recovery	Percent of Total Stainless Steel Recovered	Percent of Total Uranium Recovered
Dissolver solution[b]	64.0	93.65
Uranium recovery solution[c]	6.7	6.24
Solids	18.0	0.11
Side plates	11.3	

[a]The specimen was a section of APPR fuel element (2277 g). Clad was type 304 stainless steel; core type 302B stainless steel containing about 18% normal UO_2. Element carburized 4 hr at 950°C and homogenized 2 hr at 1100°C. Average carbon content 2.11%.

[b]Fifty liters of a 2.61 M HNO_3 and 0.3 M urea solution at 45–50°C agitated by air sparging.

[c]Three liters of boiling 10 M HNO_3.

Discussion of Results

We have demonstrated that metallurgical and chemical treatments may be combined to recover uranium from stainless steel fuel elements. Further research will be required to determine optimum conditions for the various operations. Different factors that may affect the process are discussed briefly below.

Time for Metallurgical Treatments

The time required for the metallurgical treatments is important because it will affect the number or size of the furnace units required. Tests on small specimens have shown that 2.5% C can be added to APPR fuel element material in times ranging from 4 hr at 950°C to about 0.5 hr at 1100°C. Commerical carburizing equipment operates at temperatures no higher than about 950°C, principally because higher carburizing temperatures adversely affect the steels that are ordinarily carburized. Higher

carburizing temperatures are not detrimental to APPR fuel material and their use could appreciably reduce the time required to add desired amounts of carbon. Higher carburizing temperatures, however, would create additional problems. Most important would be the stability of furnace materials at the higher operating temperatures. Higher gas-flow rates might be required to ensure uniform carburization along the length of the fuel element.

Some savings in homogenizing time may also be achieved. For most of this work we homogenized for 2 hr at 1100°C, but some results have indicated that 1-hr treatments may be adequate.

Fuel elements might be carburized and homogenized in the same furnace. Although this would eliminate one handling operation, it would also impose more severe conditions on materials for furnace liners. Use of a single furnace would require additional time for furnace temperatures to change, but this would be small if temperatures for the two treatments did not differ greatly.

Behavior of Side Plates

The side plates of the fuel element will not be carburized to the same degree as the fuel plates because of the difference in the thicknesses, which are about 0.050 and 0.030 in., respectively. Carbon will be added to the exposed surfaces at uniform rates per unit area, but the inside surfaces of the side plates are partially protected by the edges of the fuel plates and the braze metal that holds them. The carbon concentration of the side plates will therefore be $< 60\%$ that of the fuel plates. The effect of plate thickness on carburization is described in Figs. 3 and 4. The lower carbon content and greater thickness will cause the side plates to dissolve much more slowly. However, the side plates contain no uranium and therefore need not be dissolved. Baffles might be used to prevent gas flow over the outside edges of the side plates and thus decrease carburization and further decrease dissolution of the side plates. The side plates might then be removed intact from the dissolver and stored as inert solid waste. The side plates contain about 15% of the stainless steel in the APPR fuel elements.

Growth of Fuel Element

The carburizing treatment causes the fuel element to grow about 1.4% in length. The greater carbon concentration in the fuel plates causes them to grow more than the side plates. This difference in growth develops gentle waves along the length of the fuel plates, but these waves are too slight to restrict solution movement in dissolution of the fuel element.

Behavior of Fission Products

The behavior of fission products during the metallurgical treatments is not known. When specimens similar to APPR fuel elements were irradiated for 7 days at 5×10^{11} thermal neutrons$\cdot$cm$^{-2}\cdot$sec^{-1} and then heated 24 hr at 1100°C, < 0.001% of the fission products escaped during heating.[7] However, these data did not represent fuels that have been significantly damaged during irradiation. Therefore, some of the volatile fission products might be released from the fuel elements during the high-temperature treatments, and methods to prevent their escape would have to be devised.

PROCESS BASED ON INTERGRANULAR CORROSION

We examined the possibility of using intergranular corrosion to assist in the recovery of unburned uranium from spent stainless steel fuel elements. From the considerable literature on intergranular corrosion of stainless steel, metallurgical and chemical treatments were selected that might be most suitable for a uranium recovery process. These treatments were then applied to specimens of stainless steel fuel material.

Experimental Work

Metallurgical Treatments

We have studied intergranular corrosion on small laboratory tests specimens only. Specimens for tests on APPR fuel dispersions in both types 304 and 347 stainless steels were $1 \times 3 \times 0.030$ in. A few tests

---

[7] J. R. Johnson, private communication, 1955.

used 0.5 × 1.5 × 0.030-in. solid (i.e., unfueled) type 304 stainless steel specimens. Before the metallurgical treatments, the specimens were annealed in dry hydrogen at 1150°C for 0.5 hr to simulate the thermal treatment that results from brazing of APPR fuel elements. One test used specimens that had been annealed at 1200°C in an attempt to obtain large grain size.

The results of tests to add small amounts of carbon are shown in Table 5. The specimens were carburized in the Burrell furnace previously described, and carbon contents were determined by weight gain. Initially, test specimens were prepared using short carburizing times and reduced methane flow. These specimens, however, carburized more heavily on one end than the other. This effect is illustrated in Table 5 for two experiments, C-26 and C-41, in which 3-in.-long specimens were cut in half to determine the weight gain for upstream and downstream portions. To minimize this concentration gradient, we adopted a "duplex treatment" in which more uniform carburization was obtained by adding approximately one-half the desired amount of carbon, removing the specimen, reversing its position in the furnace, and carburizing it again to the desired level.

Specimens were homogenized for 2 hr at 1150°C in an atmosphere of dried helium and then withdrawn to the cool end of the furnace. During this treatment, the specimens usually lost a slight amount of weight, equivalent to a loss in carbon of 0.03% or less.

The sample were sensitized for 2 hr at 650°C in an atmosphere of dried helium or in a vacuum. Those treated in helium developed a thin oxide film on the surface, equivalent to about 0.04 mg/cm^2 or less of weight gain. This film was not removed before the chemical treatments. No weight change or oxide film was observed on specimens sensitized in vacuum.

The effect of the metallurgical treatments on the microstructure of the type 347 stainless steel fuel plate material is shown in Figs. 11 and and 12. The difference between the unsensitized and sensitized materials is barely detectable; the sensitized material shows grain boundaries that are slightly better defined. The type 304 material had appreciably larger grains, as indicated by Fig. 13.

Table 5. Results of Tests to Add Small Amounts of Carbon to Austenitic Stainless Steel or Clad Fuel Plate Specimens

Test Number	Number and Type of Specimens[a]	Temp. (°C)	Time (min)	H_2 Flow (cm^3/min)	CH_4 Flow (cm^3/min)	Carbon Added (%)	Remarks
C-1	4 304 Solid	950	30	760	170	0.47	
C-3	4 304 Solid	1000	15	760	70	0.28	
C-5a	4 304 Solid	1000	15	760	100	0.30	Double treatment.
			30	760	100	0.49	
C-5	2 304 Solid	1000	20	760	100	0.31	
	2 304 F. P.[b]	1000	20			0.44	
C-8	2 304 F. P.	1000	15	760	100	0.10	Double treatment.
			23			0.44	
C-10	2 304 F. P.	1000	21	760	100	0.22	
C-11	2 304 F. P.	1000	25	760	100	0.45	
C-13	2 347 F. P.	1000	25	760	100	0.28	
C-14	2 347 F. P.	1000	25	760	170	0.36	
C-20	2 347 F. P.	1000	40	760	170	0.53	
C-22	2 347 F. P.	1000	60	760	170	0.95	
C-23	2 347 F. P.	1000	20	760	170	0.22	
C-24	1 347 F. P.	1000	20	760	170	0.47	
C-25	1 347 F. P.	1000	15	1400	100	0.16	
C-26	1 347 F. P.	1000	20	1400	100	0.60–0.39[c]	
C-27	1 347 F. P.	1000	10(10)[d]	1400	100	0.07	
		1000	8(18)	1400	100	0.21	Ends reversed between treatments.
		1000	4(22)	1400	100	0.30	
C-28	1 347 F. P.	1000	10(10)	1400	100	0.09	
		1000	8(18)	1400	100	0.21	Ends reversed between treatments.
		1000	4(22)	1400	100	0.30	
C-29	1 347 F. P.	1000	10(10)	1400	100	0.09	
		1000	13(23)	1400	100	0.24	Ends reversed between treatments.
		1000	4(27)	1400	100	0.34	
C-30	1 347 F. P.	1000	10(10)	1400	100	0.10	Ends reversed between treatments.
		1000	8(18)	1400	100	0.27	
C-41	1 F. P.	900	12	1400	100	0.36–0.26[c]	

[a] "Solid" represents unfueled specimens; dimensions about 0.5 × 1.5 × 0.030 in. "F. P." represents fueled specimens; dimensions about 1 × 3 × 0.030 in. The first number is the number of specimens tested together.

[b] Segment of fuel plate.

[c] Specimen cut in half to ascertain carbon content of each end. First figure is for the leading specimen.

[d] Values in parentheses represent cumulative time.

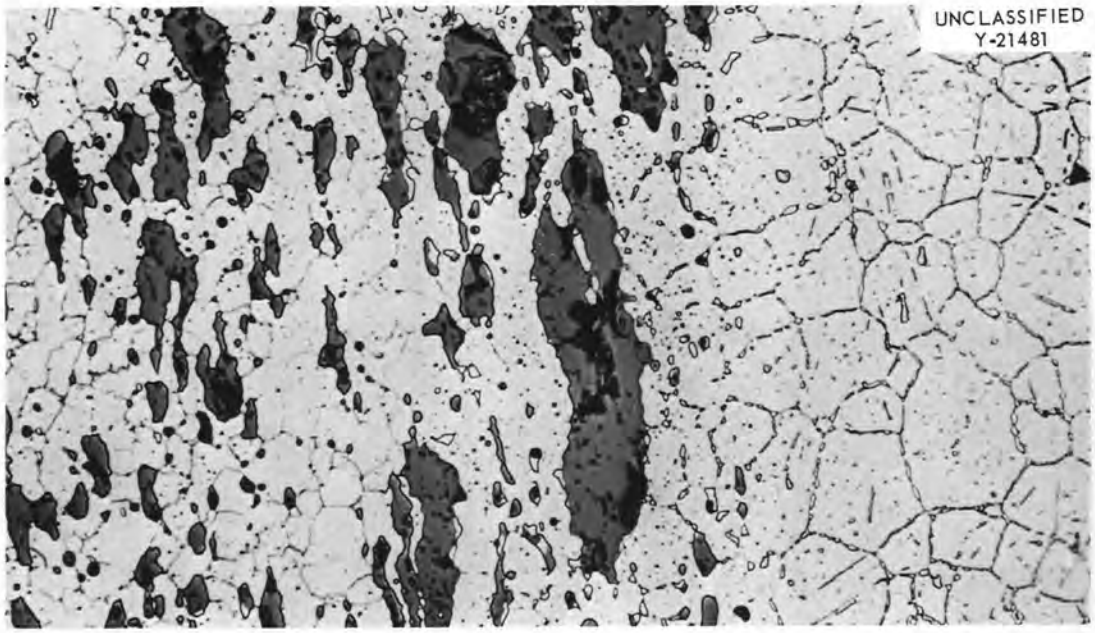


Fig. 11. Unsensitized Type 347 Stainless Steel Fueled Specimen No. C-23-1. Treatment: carburized 20 min at 1000°C to add 0.26% C; homogenized 2 hr at 1150°C. 500×.

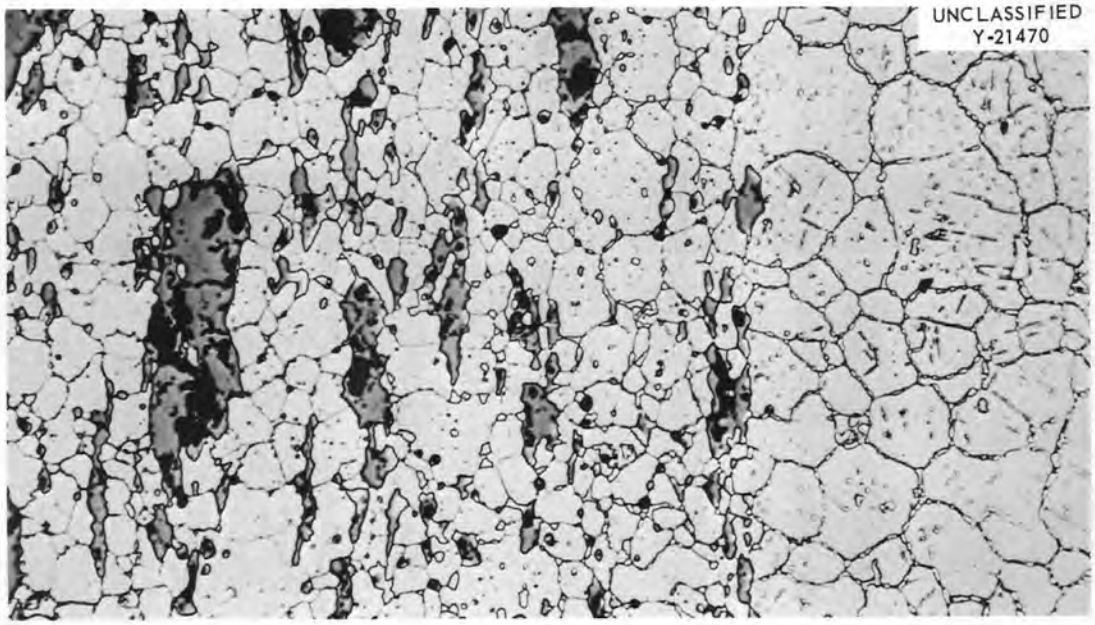


Fig. 12. Sensitized Type 347 Stainless Steel Fuel Material Specimen No. C-23-1. Treatment: carburized 20 min at 1000°C to add 0.26% C; homogenized 2 hr at 1150°C; sensitized 2 hr at 650°C. 500×.

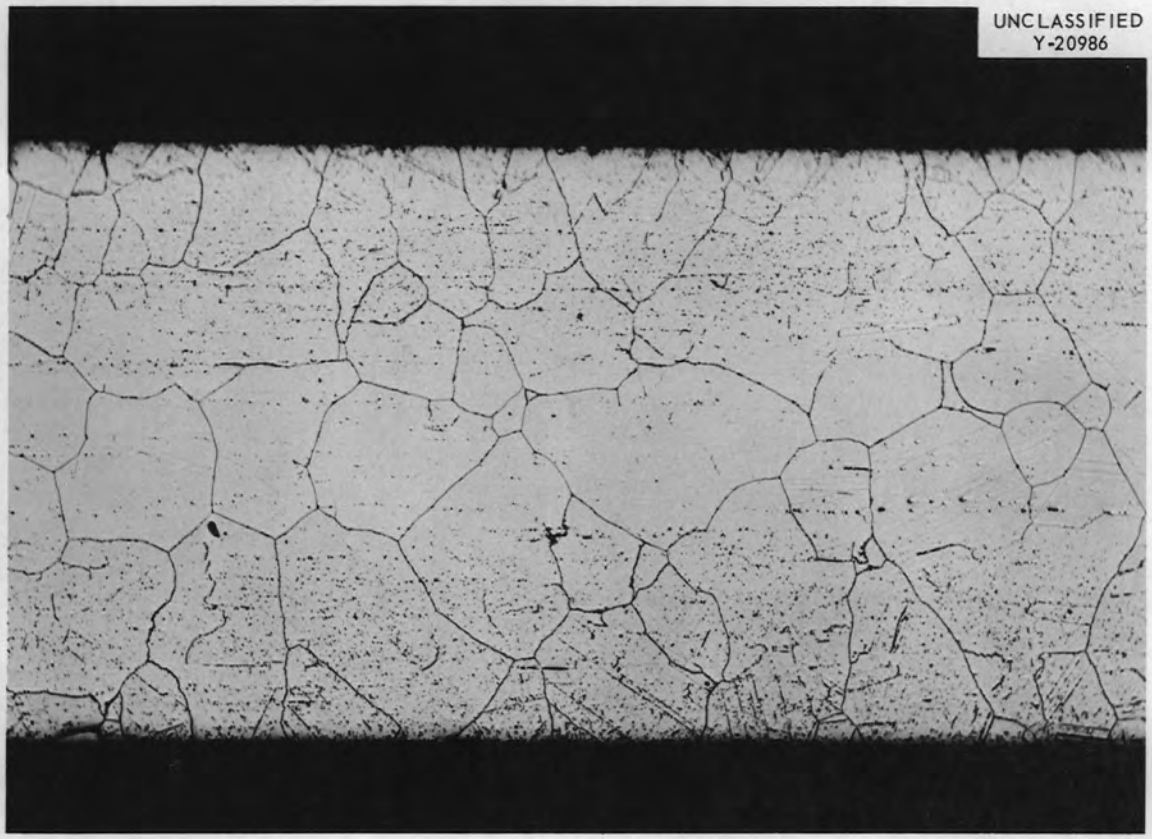


Fig. 13. Sensitized Type 304 Unfueled Stainless Steel Specimen No. C-3-2. Treatment: carburized 15 min at 1000°C to add 0.24% C; homogenized 2 hr at 1150°C; sensitized 2 hr at 650°C. 100×.

The effects of the metallurgical treatments may best be evaluated in terms of results from the tests of intergranular corrosion and uranium recovery.

Chemical Treatments

We generally tested intergranular corrosion using a solution containing 1.4 M H_2SO_4 and 0.4 M $CuSO_4$, prepared by mixing 22 ml H_2SO_4 (1.84 sp gr), 28 g $CuSO_4 \cdot 5H_2O$, and 250 ml distilled water. Also, a few tests used nitric acid solutions. The specimens were treated with refluxing solutions in glass containers while resting on edge supported by glass frames. The time for treatment ranged between 1 and 7 hr, depending somewhat on the degree of deterioration observed. Specimens became coated with copper to varying degrees during treatment with copper sulfate solutions. At the end of the tests, specimens were removed from the solution and usually stored overnight in a small volume of water. The next day the water was decanted and added to the corroding solution.

Dissolution of the uranium was tested by leaching with 10 M HNO_3 at either approximately 50°C or boiling temperature. Then the solids were washed, collected on a glass frit, dried, and weighed. The filtered wash solution was added to the leach solution. The corroding solution, the leach solution, and the solids were analyzed for uranium content, and the two solutions were usually analyzed for Fe, Ni, and Cr content.

The results of several exploratory tests to evaluate various solutions for their ability to develop intergranular corrosion on specimens of carburized and sensitized type 304 stainless steel are given in Table 6. Significant observations from these tests are listed below.

Table 6. Some Results of Exploratory Intergranular Corrosion Tests on Type 304 Stainless Steel

Specimen Number[a]	Carbon Content (%)	Solution Used	Boiling Time (hr)	Weight Loss (% of Original Sample Weight)	Remarks
C-3-1	0.23	$CuSO_4 + H_2SO_4$[b]	4.5	-	Sample easily powdered.
C-9-3	0.23	$CuSO_4 + H_2SO_4$	3	0.43	Sample easily powdered.
C-3-2	0.24	65% HNO_3	10.8	0.25	Some intergranular attack; specimen bent nearly double without any grains falling out.
C-5-3	0.31	65% HNO_3	24	2.4	Microscopic examination showed intergranular penetration to depth of 0.005 in.
C-6-2	0.20	3 M HNO_3	16.8	0.08	Some intergranular attack; specimen bent nearly double without any grains falling out.

[a]All specimens 0.030-in. thick and conditioned as follows: annealed 0.5 hr at 1150°C in hydrogen; carburized; homogenized 2 hr at 1150°C; sensitized 2 hr at 650°C.

[b]0.4 M $CuSO_4$ and 1.4 M H_2SO_4.

1. Carburization to add about 0.3% C, followed by homogenization for 2 hr at 1150°C and sensitization for 2 hr at 650°C, renders type 304 stainless steel very susceptible to intergranular corrosion.

2. Material so treated is rapidly attacked intergranularly by a boiling solution, 1.4 M in H_2SO_4 and 0.4 M in $CuSO_4$.

3. Nitric acid intergranularly attacks similar material but at a much slower rate; such attack appears to be too slow to be useful in a fuel-recovery process, but catalyzing the reaction should also be considered.

The time required to corrode solid type 304 stainless steel with the sulfuric acid-copper sulfate solutions and the ease with which the metal can be crumbled into individual grains are indicated by the data in Table 7. Treatment for 3 or 4.5 hr resulted in very fragile material and dissolved < 1% of the steel.

Table 7. Effect of Corroding Time on Intergranular Penetration of Carburized 0.031-in.-thick Type 304 Stainless Steel[a]

Time in Corroding Solution (hr)	Weight Loss[b] (%)	Examination after Test	Behavior in Pulverizing Test[c]
1	0.31	Could not be broken.	Not tested.
2	0.39	Sample easily broken.	Two small pieces not powdered.
3	0.43	Sample very fragile.	Completely powdered in 5 min.
4.5	0.62	Sample very fragile.	Completely powdered in 1.5 min.

[a]Samples were carburized 0.25 hr at 1000°C to contain 0.21–0.24% C, homogenized 2 hr at 1150°C, and sensitized 2 hr at 650°C. Testing was by boiling in a solution containing 28 g $CuSO_4 \cdot 5H_2O$, 22 ml H_2SO_4 (1.84 sp gr), and 250 ml water.

[b]In tests at 3 and 4.5 hr, some grains fell out and may have been lost.

[c]A piece about 0.5-in. square was rotated manually with several 0.63-in.-diam steel balls in a 1-in.-diam bottle.

The data from intergranular corrosion tests on specimens of APPR fuel material are shown in Table 8. Significant observations from these tests are listed below:

1. Negligible uranium dissolved in the copper sulfate and sulfuric acid corroding solution.

2. Considerably different degrees of disintegration developed in the different fuel plate materials.

3. Considerably more of the stainless steel was dissolved than in similar tests on unfueled stainless steel.

4. The amount and composition of the dissolved material showed little correlation with the known process variables.

5. The nitric-hydrofluoric acid solution rapidly attacked the steel and also dissolved most of the uranium.

The results of nitric acid leaching tests on the solids left after intergranular corrosion are shown in Table 9. These results may be summarized as follows:

1. Greater than 99% of the uranium present was leached from both types 304 and 347 stainless steel fuel materials.

2. We obtained low uranium recoveries from specimens with cores made with type 302B stainless steel.

3. Small variations in techniques or process variables affected uranium recoveries considerably.

4. The leach solutions contained between 4 and 12% of the total amount of stainless steel in the specimens.

5. A large fraction of the uranium was recovered by leaching at 50°C, but significant additional amounts were obtained by boiling.

Discussion of Results

These test results indicate that techniques based on intergranular corrosion may have unique advantages in the processing of stainless steel dispersion fuels. Principal advantages are that large fractions of the stainless steel can be retained as solid waste and the uranium-bearing solutions contain only small amounts of stainless steel components. The cost of treatment and storage of the waste products from such a processing

Table 8. Results of Intergranular Corrosion Tests on Carburized and Sensitized Fuel Plates Containing Different Stainless Steels

Specimen Number[a,b]	Material	Carbon Content (%)	Boiling Time (hr)	Uranium in Solution (% of Total Recovered)	Fe, Cr, and Ni in Solution (% of Stainless Steel Recovered)	Composition of Metals in Solution (%)			Character of Solids
						Fe	Ni	Cr	
C-3-1	304 (Unfueled)	0.23	4.5		0.28	82	15	3	Specimen very fragile.
C-5-1	304 Fuel Plates	0.44	4						Specimen not easily broken and corrosion continued.
			7	< 0.1	9	83.1	11.7	5.2	Specimen readily broken to powder.
C-8-1	304 Fuel Plates	0.39	6	< 0.12	5	82.9	12.2	4.9	Specimen readily broken to powder; plate contained very small amount of uranium; very light copper deposit.
850-8	302B Core	0.22	5	0.26[c]	4.2	93	7	0.0[c]	Light copper plate on specimen; core not readily broken.
850-6	302B Core	0.45	6	0.55[c]	6.4	85	15	0.0[c]	Copper plate on specimen; core not readily broken.
C-20	347 Fuel Plates	0.50	6	0.02	9.1	67	24	9.0	Heavy copper plate on specimen; core not readily broken.
C-27	347 Fuel Plates	0.29	5	0.006	12.0	63.1	27.4	9.5	Core not readily broken.
C-30	347 Fuel Plates	0.26[d]	5						Very little copper plate on specimen; core not readily broken; corrosion continued.
			6.5	0.005	7.6	58.8	30.8	10.4	Very little copper plate; core readily broken but did not powder.
C-28	347 Fuel Plates	0.29	2[e]	99.2[b]	56.5	71.2	12.3	16.5	Very fine powder.

[a]All specimens treated as follows: annealed 0.5 hr at 1150°C, carburized, homogenized 2 hr at 1150°C, and sensitized 2 hr at 650°C.

[b]For all specimens except specimen No. C-28, a 0.4 M $CuSO_4$ and 1.4 M H_2SO_4 corroding solution was used. For specimen No. C-28 a 4 M HNO_3 and 2 M HF solution was used.

[c]Results indicative of analytical error.

[d]Annealed 1 hr at 1200°C prior to carburization.

[e]Reaction temperature: 40–60°C.

Table 9. Results of 10 M HNO_3 Leaching Tests on APPR Fuel Material After Intergranular Corrosion Tests

Specimen Number	Core Matrix Material	Carbon Content (%)	Treatment Temperature	Treatment Time (hr)	Uranium Content of Solids (%)	Distribution of Uranium (% of Total Amount Recovered)			Distribution of Stainless Steel (% of Total Amount Recovered)		
						Solids	Leach Solution	Corroding Solution	Solids	Leach Solution	Corroding Solution
5-1	304	0.44	Boiling	3	0.28	0.9	99.0	< 0.1	82.1	11.2	6.7
8-1	304	0.39	50°C	2							
			Boiling	2	0.10–0.35[a]						4.4
850-8	302B	0.22	50–80°C	2	2.72	21.7	78.06	0.26	95.2	< 1	4.2
850-6	302B	0.45	Boiling	2	1.53	11.9	87.5	0.55	91.2	2.4	6.4
C-20	347	0.50	50°C	3							
			Boiling	1	1.02	5.32	94.66	0.02	81.8	9.1[b]	9.1
C-27	347	0.29	50°C	2			81.56			0.3	
			Boiling	2	0.069	0.37	99.62[b]	0.006	80.6	7.4[b]	12.0
C-30	347	0.26	50°C	2			54.40			0.1	
			Boiling	2.5	0.14	0.70	99.30[b]	0.005	88.8	3.6[b]	7.6
C-28	347	0.29	Boiling	1	0.0037	0.01	0.79[b]	99.2[c]	42.1	1.4	56.5

[a] Uranium content of material passing 1/16-in. mesh screen (9.4 g) = 0.10% U; uranium content of material retained on 1/16-in. mesh screen (1.0 g) = 0.35% U.

[b] Includes amount from 2-hr leaching treatment at 50°C.

[c] Intergranular corrosion obtained in 4 M HNO_3 + 2 M HF solution.

scheme may be less than those for other processes presently being considered, and the resulting solid residue may be more suitable for permanent waste disposal.

The experimental data are not sufficient to define the extent to which the different process variables affect the time required for processing, the uranium recoveries obtainable, or the ultimate storage volumes. However, the fact that promising results were so easily obtained indicates that additional work to define optimum conditions for the different process variables could very likely lead to results better than those reported here.

The following discussion considers the available data and the different process variables from the aspect of possible improvements in the process.

Metallurgical Variables

Fuel Plate Material. The data indicate that type 304 stainless steel disintegrates into individual grains of metal more readily than does type 347. However, slightly different treatments may produce similar disintegration of type 347. On the other hand, the difference in degree of disintegration may be an inherent characteristic dependent on composition or grain size of the steel. In such an event, easier processing might be a factor favoring the use of type 304 stainless steels for fuel elements.

Grain Size. The uranium dioxide dispersed through the core material of the fuel plate generally exists at the grain boundaries of the core matrix, as indicated in Fig. 11. If all of the uranium is to be exposed by intergranular corrosion, a major fraction of the grain edges must be attacked. Although large-grained steels suffer more than fine-grained steels from intergranular attack, to increase the grain size of the core material by metallurgical treatments probably will not be feasible. Even if such grain growth could be induced, some of the small uranium dioxide particles could be locked within the grains and thus would not be exposed by the intergranular corrosion treatment. The grain size of the core material, therefore, does not appear to be a variable that could be changed by heat treatment to improve a recovery process based on intergranular corrosion.

Carbon Content. The data indicate that variations in carbon content between about 0.2 and 0.6% have little effect on the uranium recoveries obtained. However, we obtained the most rapid intergranular corrosion on samples of unfueled stainless steel containing 0.23% C and the best uranium recovery on samples containing 0.26% C. Excess carbides existing within the grains are reported to act as nuclei on which carbon in solution may precipitate (See Appendix B). The presence of such nuclei may reduce the amount of carbon available for grain-boundary precipitation and thus may reduce the amount of chromium depletion at the grain edges. Consequently, the optimum amount of carbon may not be the maximum amount soluble at the homogenizing temperature, but instead, it might be the maximum amount that is retained in solid solution prior to sensitization. We suggest that future work should investigate the behavior of steels with lower carbon contents.

Homogenizing Temperature and Time. The function of the homogenizing treatment is to take the carbon into solid solution and allow it to diffuse uniformly through the steel. A 2-hr treatment at 1150°C is apparently adequate. Appreciable carbide precipitates during cooling from the homogenizing temperature, and small differences in cooling rate may considerably affect the behavior of the steel. The rate of cooling from the homogenizing temperature may not have been controlled sufficiently in these tests. Specimens were cooled by moving them to the cold end of the furnace. When a specimen was treated alone, it cooled quite rapidly. However, when four specimens were treated together, cooling was slower because of the greater heat content and because the specimens were moved more slowly to reduce thermal shock to the furnace tube. We estimate that cooling times from 1150°C to room temperature might have varied from about 5 to 15 min in the different tests. The time-temperature relations during cooling are of course not known. We suggest that in future work specimens be rapidly removed from the furnace and quenched, so that carbide precipitation will be more completely influenced by the sensitizing treatment.

Sensitizing Temperature and Time. Sensitization treatments were not intentionally varied. Different steels may require different treatments for optimum sensitizing. The possibilities of obtaining sufficient carbide

precipitation through control of the cooling rate from the homogenizing treatment should also be considered, so that the sensitizing treatments may not be necessary.

Chemical Variables of Intergranular Corrosion

Type of Corroding Solution. The 0.4 M $CuSO_4$-1.4 M H_2SO_4 solution has given good results in tests thus far. Nitric acid, catalyzed with hydrofluoric acid, may also be of interest if very low fluoride concentrations can be used. After optimum metallurgical treatments have been developed, further consideration may be given to other chemical solutions for causing intergranular corrosion.

Concentration of Reactants and Solution Volume. For a workable recovery process based on corrosion in the acidified copper sulfate solution, the volume of solution required for producing intergranular corrosion is of considerable importance. The solution will probably dissolve some fission products and thus will require permanent storage. The exact mechanism by which the corroding solution reacts with the metal is not understood, but presumably it is a combination of dissolution in sulfuric acid and a replacement reaction with the copper sulfate. Since the amount of copper that deposits on the specimens during the corroding reaction has varied considerably from one test to another, the extent to which the two reactions are involved appears to depend on the metallurgical characteristics of the steel. Regardless of the mechanism of the reactions, the rate of intergranular corrosion will likely be influenced by the relative concentrations of the reactants and the reaction products in the solution. The reactions will therefore be affected by the relations between the volume of the corroding solution and the amount of steel dissolved. These factors have not been investigated thus far; their effect has been minimized by using relatively large volumes of corroding solution.

Reaction Time. The time allowed for intergranular corrosion in these tests was determined to some extent by the degree of deterioration of the specimens but was also limited to 6 or 7 hr. We based this arbitrary limit on an acceptable maximum time for a recovery process. In future work, the effect of time on the progress of the dissolution reaction should be studied

to ensure that the reaction proceeds to completion. Such a technique should permit the effects of the different process variables to be more accurately interpreted.

Variables Affecting Uranium Dissolution

The uranium exposed by the intergranular corrosion treatment is readily dissolved in boiling nitric acid. Therefore, no significant improvement in the recovery process should result from variations in the acid concentration, leaching temperature, or leaching time. The leaching treatment also has dissolved varying amounts of stainless steel. However, stainless steel containing small amounts of carbon reacts very slowly with nitric acid, and the leaching treatments should not be expected to expose additional uranium. The uranium recoveries might be improved through the use of mechanical agitation and the use of improved techniques for washing the solids.

ACKNOWLEDGMENTS

The idea of using carbon additions to facilitate processing of stainless steel fuels was originated by J. H Frye, Jr., Director, Metals and Ceramics Division. His guidance and the direction of J. L. Gregg, E. J. Boyle, and J. E. Cunningham were helpful in the work. Much of the experimental work was done by R. A. Padgett and his careful assistance is much appreciated. Metallographic work was done by C. Mathes and others under the direction of R. J. Gray. Chemical analyses were made under the direction of J. H. Edgerton and W. R. Laing. The suggestions and assistance of J. E. Savolainen, J. H. Goode, and R. E. Blanco of the Chemical Technology Division were instructive and appreciated.

We acknowledge the assistance of Sigfred Peterson for revision of the manuscript and the Metals and Ceramics Reports Office, under the direction of Meredith Hill, for typing and processing the report.

APPENDIX A

Behavior of Carbon in Stainless Steel

The extent to which the passivity of stainless steel can be destroyed by carbon will depend on the manner in which the carbon and chromium combine. In alloys of Fe, C, and Cr, the following carbides are known to exist:

1. $Cr_{23}C_6$ – pure chromium carbide; contains 5.68% C.
2. $(CrFe)_{23}C_6$ – iron dissolved in chromium carbide; contains more than 70% Cr and about 6% C.
3. $(CrFe)_7C_3$ – iron dissolved in chromium carbide; contains more than 36% Cr and about 9% C.
4. $(FeCr)_3C$ – chromium dissolved in iron carbide; may contain up to 15% Cr.
5. Fe_3C – pure iron carbide; contains 6.69% C.

None of these carbides except the pure carbides of iron and chromium are stoichiometric compounds. In the mixed carbides $(CrFe)_7C_3$ and $(FeCr)_3C$, the ratio of carbon atoms to metal atoms increases slightly with the chromium content.

The manner in which carbon and chromium combine and precipitate from the austenitic solid solution in type 304 stainless steel depends on the carbon content and the thermal history of the steel. Approximately 0.3% C is soluble in type 304 stainless steel at 1100°C while < 0.03% C is soluble at room temperature. Thus, a steel with about 0.1% C will contain precipitated carbides if it is cooled slowly from 1100°C to room temperature. If cooled rapidly, the carbon may be retained in supersaturated solid solution, but carbides can be precipitated by subsequent heating. Carbide precipitation is time and temperature dependent and has been the subject of many research investigations.

Upon reheating annealed stainless steels containing 0.07% C, Kinzel[8] found that carbon diffuses to the grain boundaries and forms an intergranular precipitate of chromium carbide, $Cr_{23}C_6$. Chromium diffuses much more slowly than carbon; so the chromium to form the carbide apparently comes only from the outside edge of the grains.

---

[8]A. B. Kinzel, Trans, Am. Inst. Mining Met. Engrs. 194, 469 (1952).

The behavior of stainless steels containing in excess of about 0.3% C is less clearly defined. Figure 14 shows the equilibrium carbides present in slowly cooled Fe-Cr-C alloys.[9] Since nickel does not form carbides, similar carbides may be presumed to occur in carburized austenitic stainless steel. In steels containing about 19% Cr and 0.3 to 0.8% C, the equilibrium carbide is $(CrFe)_{23}C_6$, which contains over 70% Cr. With carbon in excess of 0.9%, the stable carbide is $(CrFe)_7C_3$, which contains over 36% Cr and may contain up to 55% Fe. As the amount of carbon increases or as chromium is depleted from the matrix phase by combination with carbon, excess carbon presumably will form iron carbide, $(FeCr)_3C$, which may contain up to 15% Cr. Similar relationships were reported by Kuo[10] after studying the equilibrium structures in Fe-Cr-C alloys at 700°C. He found that Fe_3C may change to $(CrFe)_7C_3$. This reaction apparently occurs in two stages: (1) the concentration of chromium in Fe_3C to form a solid solution of $(FeCr)_3C$ to its maximum solubility limit of 15% Cr and (2) the transformation of the $(FeCr)_3C$ solid solution into $(CrFe)_7C_3$. Similar behavior may allow $(CrFe)_7C_3$ to transform into $(CrFe)_{23}C_6$, as was noted by Lane and Grant.[11]

Thus, as the amount of carbon added to stainless steel is increased, the carbides that are formed become increasingly richer in iron. Small amounts of carbon remove chromium quite efficiently from the matrix phase, but large amounts of carbon must convert a considerable fraction of the metal to carbides before all of the chromium is combined with carbon.

Stainless steels can be carburized to contain considerably more carbon than the amount soluble at the carburizing temperature, and the carbon can be diffused uniformly through the steel. Specimens have been prepared containing up to 5.7% C.

Because of the complexity of carbide formation, we could not predict the amounts of carbon required to destroy the corrosion resistance of the metal and thus obtain optimum dissolution rates. We investigated the effect

---

[9]R. M. Brick and A. Phillips, Structure and Properties of Alloys, 2nd ed., McGraw-Hill, New York, 1949.

[10]K. Kuo, J. Iron Steel Inst. (London) 173, 363 (1953).

[11]J. R. Lane and N. J. Grant, Trans. Am. Soc. Metals 44, 113 (1952).

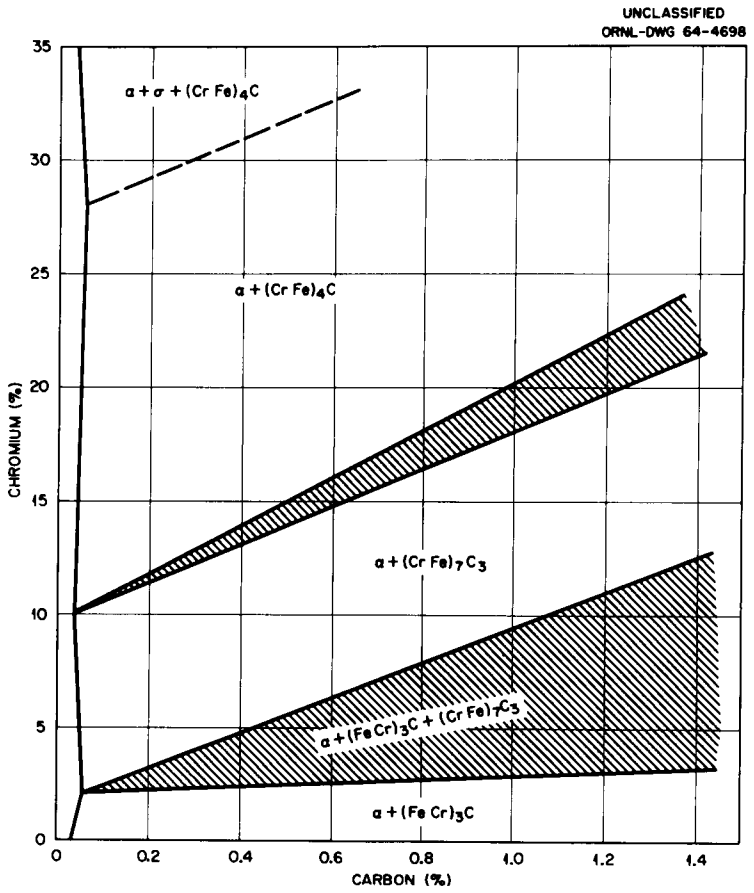


Fig. 14. Diagram Showing Phases Present in Slowly Cooled Fe-Cr-C Alloys as a Function of Chromium and Carbon Content. From Structure and Properties of Alloys, 2nd ed., by R. M. Brick and A. Phillips. Copyright 1949. McGraw-Hill Book Company. Used by permission.

of carbon content on dissolution rate experimentally. The composition of the carbides left after some experiments was obtained from chemical analyses of the residue after dissolution of the matrix phase of carburized and homogenized stainless steel. Typical results are shown in Table 10.

Table 10. Chemical Analyses of Carbides Remaining After Dissolution of Matrix Phase of Type 304 Stainless Steel

Constituent	Carburized Samples 88D[a] (%)	Fuel Element Carburized in Test No. 4[b] (%)
Cr	46.8	38.4
Fe	41.0	31.6
C	9.0	6.9
Mn	1.8	
Ni	0.9	0.8
SiO_2		6.4
H_2O		10.9
	99.50[c]	95.0[d]

[a]Treatment: carburized to contain 2.81% C; homogenized for 2 hr at 1100°C; boiled for 2 hr in 2 M HNO_3.

[b]Treatment: carburized for 4 hr at 950°C to contain 2.3% C; homogenized for 2 hr at 1100°C; treated for 6.5 hr in 2.61 M HNO_3 at 50°C; residue boiled for 4 hr in 10 M HNO_3.

[c]Balance due to silicon and analytical error.

[d]Balance due to B, Mn, P, U, and analytical error.

APPENDIX B

Variables Affecting Intergranular Corrosion

Intergranular corrosion of austenitic stainless steels has been studied in the development of methods for avoiding such corrosion. The literature has been reviewed and is discussed briefly below.

Susceptibility to intergranular attack in sensitized stainless steels is quite generally attributed to the precipitation of chromium carbide at the grain boundaries of the metal. This develops a chromium-depleted layer on the edges of the stainless steel grains, and this layer readily reacts with, and dissolves in, certain corroding solutions. Although the low chromium content of the grain edges is thought to be largely responsible for its poor resistance to chemical attack, this factor alone cannot explain completely the results that have been obtained. Kinzel[12] considers that the atomic disregistry between the metal grain and the carbide may be largely responsible for rapid intergranular attack.

The relation between carbon content and maximum susceptibility to intergranular corrosion of stainless steel has been studied by Monypenny[13] and by Bain, Aborn, and Rutherford.[14] They found the severity of intergranular corrosion to increase with carbon content up to about 0.2% C, the maximum investigated. However, the effectiveness of carbide precipitation in promoting intergranular attack is reported to decrease if undissolved carbides exist within the grains.[13] Such undissolved carbides may act as nuclei upon which dissolved carbon could precipitate and therefore would reduce the amount of carbon available for precipitation at the grain boundaries. Thus, to ensure maximum corrosion, the carbon in the steel should at least be limited to the content that is completely soluble in the steel at the homogenizing temperature and possibly to the content that is retained in solid solution before sensitization.

The sensitizing time and temperature also have an important effect on the degree of susceptibility to intergranular corrosion. The relations

---

[12]Kinzel, op. cit.

[13]J. H. G. Monypenny, Stainless Iron and Steel, 1 and 2, 3rd ed., Chapman and Hall, London, 1951.

[14]E. C. Bain, R. H. Aborn, and J. J. Rutherford, Trans. Am. Soc. Steel Treating 21, 481–509 (1933).

between these factors for a steel containing 0.08% C have been determined by Bain et al.[14] and are shown in Figs. 15 and 16. The apparent recovery from sensitivity to intergranular attack that occurs on prolonged heating at temperatures above 650°C is explained either by agglomeration of the carbides and diffusion of chromium from the body of the grains or by stress relief that destroys the disregistry at the metal-carbide interface. Similar conclusions were drawn by Mahla and Nielsen[15] and by Gillmore[16] for steels tested in boiling nitric acid.

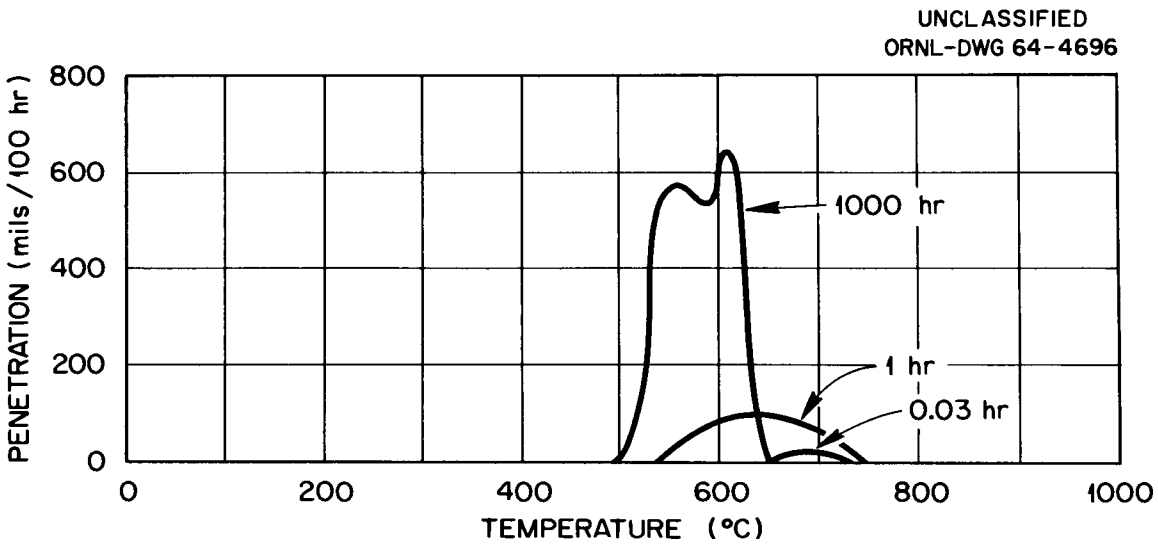


Fig. 15. Sensitivity, Measured as Penetration in 100-hr Corrosive Attack, as Developed in Stainless Steel Specimens Heated for Various Times at a Series of Constant Temperatures. Steel composition: 18.1% Cr, 8.9% Ni, 0.08% C. Corrodant: 47 ml H_2SO_4 (sp gr 1.84) and 13 g $CuSO_4 \cdot 5H_2O$ per liter. From E. C. Bain, R. H. Aborn, and J. J. Rutherford, "The Nature and Prevention of Intergranular Corrosion in Austenitic Stainless Steels," Trans. Am. Soc. Steel Treating 21, 481–509 (1933).

---

[15]E. M. Mahla and H. A. Nielsen, Trans. Am. Soc. Metals 43, 290 (1951).

[16]R. N. Gillmore, Iron Age 168, 81 (1951).

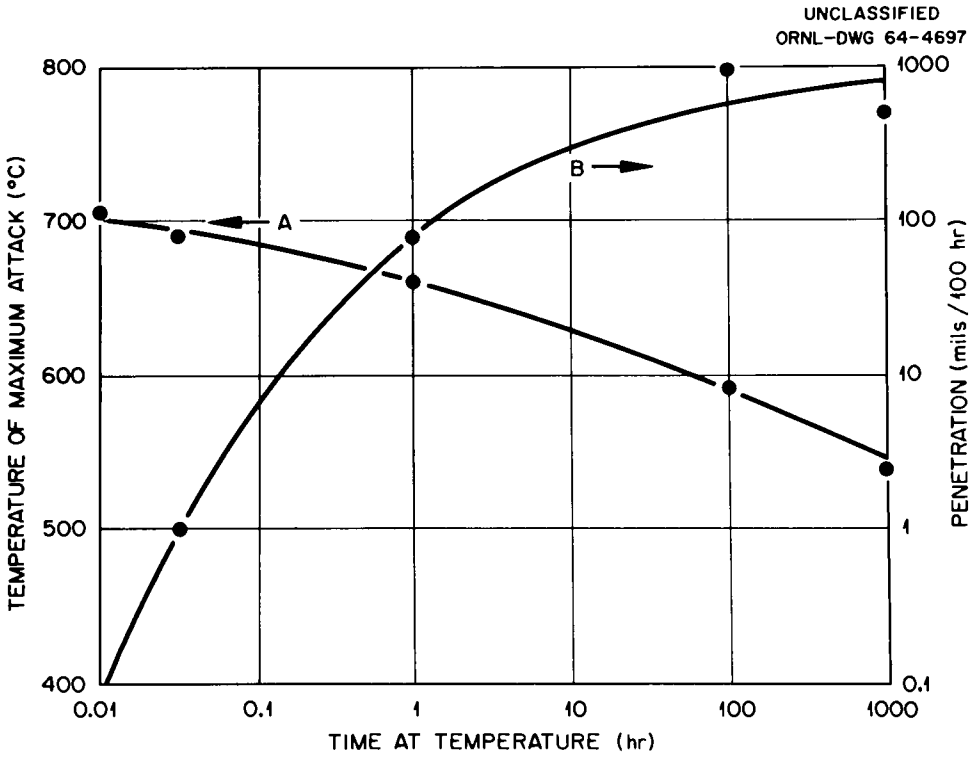


Fig. 16. (A) Time of Heating at Various Temperatures to Produce Maximum Susceptibility to Intergranular Attack and (B) Maximum Rates of Penetration so Obtained. Carbon content, 0.08%. Corrodant: 47 ml H_2SO_4 (sp gr 1.84) and 13 g $CuSO_4$ per liter. From E. C. Bain, R. H. Aborn, and J. J. Rutherford, "The Nature and Prevention of Intergranular Corrosion in Austenitic Stainless Steels, Trans. Am. Soc. Steel Treating 21, 481–509 (1933).

Other factors being constant, intergranular corrosion is reported to be a more serious problem in coarse-grained steel than in fine-grained steel.[13,14]

The chemical composition of the steel may significantly affect the degree to which susceptibility to intergranular corrosion may be developed. The types 347 and 321 stainless steels, which contain niobium or titanium, have been developed to reduce sensitivity when welded. These steels contain about 0.08% C as an impurity, and the carbon preferentially combines with niobium or titanium, so that little carbon is available to combine with the chromium. Since these additives are effective only when present in amounts approximately ten times the carbon content, the resistance conferred by niobium or titanium can be destroyed by adding excess carbon. Steels containing about 2% Si or Mo also resist intergranular attack.[13]

The mechanism of protection of these elements is obscure, but it is thought that ferrite forms and alters the effect of carbide precipitation.

The degree and rate of intergranular attack also depend on the corroding solutions and chemical treatments used. Many solutions may cause intergranular attack on sensitized stainless steel. Various mixtures of sulfuric acid and copper sulfate are most frequently used to study resistance of steels to intergranular attack, and the behavior of these solutions is discussed by Monypenny.[13] A solution containing 47 ml of H_2SO_4 and 13 g of $CuSO_4 \cdot 5H_2O$ per liter is reported to be more rapid in its attack than a solution containing 47 ml of H_2SO_4 and 111 g of $CuSO_4 \cdot 5H_2O$ per liter, but attack by the more dilute solution is also more sensitive to variations in test conditions.

Theoretical aspects of chemical factors affecting intergranular corrosion of sensitized stainless steels are discussed by Rocha.[17] Briefly, he considers that intergranular corrosion is an electrochemical phenomenon arising from differing electrode potentials between the high-chromium bodies of the grains and the chromium-depleted grain edges. The oxidation potential of the sulfuric acid and copper sulfate solution is maintained by the copper sulfate in a range that causes the chromium-depleted edges to dissolve but does not allow reaction with the higher chromium material. Also, intergranular corrosion may be accelerated by adding zinc dust or hydrazine sulfate to the corroding solution. Such additions quickly adjust the oxidation potential of the solution to values most suitable for producing the intergranular attack.

Boiling concentrated nitric acid also intergranularly attacks sensitized stainless steels containing about 0.07% C. However, available information indicates that such attack is considerably slower than can be achieved with the acidified copper sulfate solutions.

Nitric acid corrosion of annealed austenitic stainless steel is discussed by Evans,[18] who found that such corrosion depends critically on

---

[17] H. J. Rocha, Stahl Eisen 70, 608 (1950).

[18] T. E. Evans, Nitric Acid Corrosion and Polarization of Austenitic Stainless Steels – Effect of Added Species, UKAEA Report IGR-TN/C.419 (Nov. 1956).

the oxidation potential of the solution. The presence of small amounts of certain ions in solution accelerated the corrosion under certain conditions, but this accelerated corrosion was inhibited by strong beta-gamma irradiation.

Rapid intergranular attack also has been obtained on sensitized stainless steel with a pickling solution containing about 25% HNO_3 and 2% HF.

APPENDIX C

Details of Carburizing Full-Size Fuel Elements

Since no large carburizing furnace was available, full-size elements were carburized in a gas-tight, 0.25-in.-thick box of type 310 stainless steel. The fuel element was held in place by spacers, leaving 0.25 in. of space for gas flow at the top, bottom, and sides of the fuel element. The carburizing gas entered the box through a 1-in.-diam tube at the center of the inlet end of the box, about 5.5 in. from the fuel element. Two diffuser plates, 1.5 in. apart and each containing 16 evenly spaced 0.25-in.-diam holes, were used to break up the inlet gas stream to make the gas flow more uniform across the cross section of the fuel element. The carburizing gas exhausted at the other end of the box through a 1-in.-diam tube in the top of the box. The exhaust gas was led out of the furnace and burned as it left a 0.19-in.-diam nozzle.

To form the carburizing atmosphere, dried bottled hydrogen and bottled methane were mixed on entering a T-joint about 5 ft from the inlet to the carburizing box. Flow meters measured the gas flow. Dried helium was used as a purge and as an inert atmosphere during cooling.

To test the carburizing atmosphere, samples of the inlet and exhaust gases were obtained from later tests and analyzed with a mass spectrometer. In the inlet line, gas samples were obtained from a tap that was about 2 ft downstream from the mixing T. Samples were collected by evacuating the sample bottle and tap connection with a mechanical vacuum pump, then closing a valve in the pump line, and finally slowly opening a valve connecting to the lines carrying the gas mixture.

The carburizing box containing the fuel element was heated in a muffle furnace during carburizing. The furnace door, left partially open to accommodate the inlet and exhaust tubes, was blocked up with insulating brick. Even so, the temperature throughout the fuel element was not uniform because of excessive heat losses through the front of the furnace. In some tests, a considerable draft further cooled the front of the furnace. Fuel element temperatures were measured by three Chromel-Alumel thermocouples placed between center plates and located to indicate temperatures near the inlet end, center, and exhaust end of the fuel element.

The small type 304 stainless steel specimens at each end of the fuel element were 0.031 in. thick and were suspended between the top and bottom plates of the fuel element. The sides of these specimens were parallel to the gas flow, and their edges were about 0.5 in. from the ends of the inner fuel plates. The fuel element used in test 4 had fuel plates containing a total of 384 g of depleted uranium dioxide; the fuel plates for the other three elements were of unfueled type 304 stainless steel.

ORNL-2398
UC-25 — Metals, Ceramics, and Materials
TID-4500 (34th ed.)

INTERNAL DISTRIBUTION

1-3. Central Research Library
4. Reactor Division Library
5-6. ORNL — Y-12 Technical Library
Document Reference Section
7-26. Laboratory Records Department
27. Laboratory Records, ORNL R.C.
28. ORNL Patent Office
29. R. E. Adams
30. E. S. Bomar
31. J. A. Burka
32. G. A. Cristy
33. W. H. Cook
34. F. L. Culler
35. J. E. Cunningham
36. J. L. English
37. L. M. Ferris
38. R. B. Fitts
39. J. H Frye, Jr.
40. R. J. Gray
41-45. M. R. Hill
46. H. Inouye
47. C. E. Larson
48. T. S. Lundy
49. H. G. MacPherson
50. J. R. McWherter
51. S. Peterson
52. J. B. Ruch
53. W. G. Stockdale
54. J. A. Swartout
55. R. E. Thoma
56. D. B. Trauger
57. C. D. Watson
58. A. M. Weinberg
59-78. G. D. Whitman
79. M. B. Bever (consultant)
80. A. A. Burr (consultant)
81. J. R. Johnson (consultant)
82. A. R. Kaufmann (consultant)

EXTERNAL DISTRIBUTION

83. C. M. Adams, Jr., MIT
84-85. D. F. Cope, AEC, ORO
86. G. L. Gregg, Bard Hall, Cornell University
87. L. P. Hatch, Nuclear Engineering Department, BNL
88. J. Simmons, AEC, Washington
89. E. E. Stansbury, University of Tennessee
90. D. K. Stevens, AEC, Washington
91. Research and Development Division, AEC, ORO
92-675. Given distribution as shown in TID-4500 (34th ed.) under Metals, Ceramics, and Materials category (75 copies — CFSTI)