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GRAPHITE-STAINLESS STEEL COMPATIBILITY STUDIES

B. Fleischer
J. H. DeVan
J. H. Coobs

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ABSTRACT

The compatibility of type 304L stainless steel in intimate contact with graphite is being studied as a function of temperature and contact pressure. This study is an outgrowth of materials compatibility problems in present and advanced gas-cooled reactors, where structural members in direct contact with graphite provide the possibility of both carburization and self-welding.

Initial studies have been concerned with surface reactions in the absence of gaseous contaminants under a vacuum of 10^{-6} mm Hg at temperatures from 540 to 705°C. Stainless steel specimens are pretreated to provide three surface conditions: hydrogen-fired, preoxidized, and copper-plated. Surface contact pressures have ranged from 0 to 10,000 psi.

Test results are presented which establish the lower temperature limit for significant diffusion between graphite and stainless steel at approximately 600°C. Above this temperature, diffusion between untreated or hydrogen-fired stainless steel surfaces was found to effect complete bonding of the two materials at contact pressures as low as 500 psi. Bonding was effectively prevented by the presence of either an oxide film or a copper plate at temperatures up to 700°C. Where bonding occurred, diffusion rates measured for carbon in stainless steel were comparable with those reported for stainless steel in carbon-saturated sodium. However, phases produced in surface reactions between graphite and stainless steel were of higher order than those reported for the sodium carrier.

Lack of carburization in control specimens not in contact with graphite indicated the role of the gas phase to be unimportant at impurity pressures of 10^{-6} mm Hg.

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Advanced reactors employing graphite as a moderator in high-temperature environments give rise to compatibility problems involving structural metal parts in intimate contact with graphite. Extended operation presents the possibility of bonding and carburization of these structural members. The purpose of this investigation is to determine the extent of these problems and to study methods of minimizing or circumventing them.

REVIEW OF RELATED STUDIES

The work of several previous investigators has verified that a compatibility problem does indeed exist. For instance, while working at 1040°C, Giacobbe[1] produced extensive carburization of types 304 and 316 stainless steels after only 1 hr at temperature. Intimate contact between graphite and metal was produced at room temperature by placing graphite in a tube and collapsing the tube walls on the graphite by use of controlled external loads. The tube was evacuated to approximately 2×10^{-4} mm Hg for 6 hr prior to compression of the tube walls, and the vacuum was maintained throughout the compression operation and heating cycle. His investigations revealed that the gas phase plays an insignificant role in the carburization reaction, that the presence of an oxide film drastically reduces the rate of carbon absorption, and that carbon absorption increases with increasing contact pressure between the graphite and metal. Giacobbe explained the increased absorption by his "theory of contact catalysis," which postulates that "when molecules or atoms are adsorbed at a surface, the energy of activation is lowered for the

[1]J. B. Giacobbe, "Mechanism of the Carburization of Some Stainless Steels," Trans. Am. Soc. Metals 45, 134-150 (1953).

formation of new compounds, e.g., alloy carbides." He expressed the opinion that the higher contact loads serve to bring more graphite into contact with the metal, thus increasing the amount adsorbed.

More recently, Gerds and Mallett[2] investigated a number of pure metals and alloys in contact with graphite in the range 900 to 1010°C. In their procedure the graphite and metal disks were sealed inside a small stainless steel cup by a cap welded on the cup in an argon-filled dry box, and a dead-weight load was then applied to the capsule at temperature to yield an apparent stress of 2000 to 3000 psi. They used metallographic and hardness studies to evaluate Mo, Cu, Ni, Nichrome V, Inconel, Inconel X, Alnicro, type 316 stainless steel, type 318 stainless steel, and type 316 stainless steel plated with either nickel, copper, or chromium. Gerds and Mallett found that, after 1000 hr, all alloys were considerably carburized at 1010°C and that at 900°C Inconel X was slightly carburized but Alnicro and type 316 stainless steel were considerably carburized. They reported that an 8-mil copper foil on Inconel X prevented significant carburization at 1010°C and that an 8-mil copper plate or as little as 2.5 mils of chromium plate prevented carburization of type 316 stainless steel at 900°C.

The results of extensive tests on graphite-metal compatibility for the Maritime Gas-Cooled Reactor program have been reported by Bokros.[3] Working in the 705–925°C range, he evaluated Mo, Nb and Nb alloys, Ni and Ni-Cu alloys, austenitic and ferritic stainless steels, an Fe-Cr-Al alloy, Ni-Cr-Fe-Mo alloys, and various protective coatings. Intimate contact between graphite and metal was obtained through application of a dead-weight load to a stack of metal and graphite disks to produce an apparent stress of 2000 psi. Graphite dies were used to support and contain the specimen stacks. The entire system was evacuated and degassed at 485°C and then filled with helium (99.995% pure) prior

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[2]A. F. Gerds and M. W. Mallett, "Compatibility of a Number of Metals and Alloys with Graphite," Trans. Am. Soc. Metals 52, 1027–1042 (1960).

[3]J. C. Bokros, Graphite-Metal Compatibility at High Temperatures, General Dynamics Report GA-782 (June 1959).

to testing. Even so, impurities in the helium – N_2, H_2, CO, and CO_2 – from outgassing of the graphite during the test reached 4 mole %. In some tests the impurity levels were reduced by zirconium gettering.

Bokros' results showed that significant reaction occurred with most of the metals at 925°C, with the most resistant being nickel, Monel, and type 430 stainless steel. Some metals carburized at temperatures as low as 705°C, among them Nichrome V, Inconel, Inconel X, Inconel 702, and types 304, 347, 330, and 310 stainless steels. Outgassed impurities in the helium apparently performed a significant role in the carburizing reaction. However, even when the impurity level was low, carburization still occurred, thus indicating that solid-state carburization was present.

Carburization tendencies of type 304 stainless steel were also studied by Anderson and Sneesby,[4] who used liquid sodium saturated with an excess of powdered carbon as the carburizing medium. They determined distribution of carbon in the metal by chemical analysis, metallographic examination, and hardness measurements and calculated the diffusion coefficients. Using these data, they calculated the approximate depths of the carburized layers as a function of time at temperature for a series of temperatures.

Anderson and Sneesby observed that the reactions between liquid sodium, carbon, and steel proceeded rapidly to equilibrium and determined that the carbon content of a type 304 stainless steel surface in equilibrium with carbon-saturated sodium varied from approximately 2.7% at 540°C to > 4% at 870°C. During their examination of carburized specimens, only one complex carbide, $(Cr,Fe)_7C_3$, was identified. They calculated that the depths of the carburized layer produced in 1000 hr varied from < 3 mils at 540°C to approximately 50 mils at 815°C.

In addition to the foregoing, tests of a preliminary nature were made at the Oak Ridge National Laboratory.[5] Metal specimens were

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[4]W. J. Anderson and G. V. Sneesby, Carburization of Austenitic Stainless Steel in Liquid Sodium, NAA-SR-5282 (Sept. 1, 1960).

[5]GCR Quar. Progr. Rept. Dec. 31, 1959, ORNL-2888, pp 145–150.

strapped tightly to the sides of graphite blocks at room temperature and exposed to circulating helium at 760°C. Figure 1 shows the results of exposing type 304 stainless steel in contact with graphite to an atmosphere containing a high level of impurities outgassed from the graphite. It is evident that considerable bonding and carburization occurred. In a similar test at 760°C, T-1 steel in contact with graphite was decarburized;[6] however, the helium atmosphere in this test was relatively free of outgassed impurities.

PRESENT INVESTIGATION

The earlier results[1–5] plus the somewhat inconsistent nature of Bokros' results at 705°C did little to clarify the effect of temperature, contact pressure, and atmosphere on the compatibility of structural metals and graphite in the range 540 to 705°C. Also, Giacobbe's allusion to solid-state adsorption of graphite on metal raised considerable apprehension concerning the mechanism of the reactions. The present investigation was therefore designed to resolve these problems and to better understand the processes involved. Specifically, the dependence of carburization on temperature, contact pressure, and atmosphere is being determined, and protective coatings are being evaluated. In the studies reported here the tests were conducted in the absence of gases in order to isolate the solid-state reaction. The mechanism of the reactions, reaction rate, and carbon diffusion will be studied later. In the study of the mechanism of the reactions the effect of gases such as CO, CO_2, H_2, H_2O, and CH_4 on the compatibility of graphite and type 304 stainless steel will be determined.

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[6] J. H. DeVan, "Reactions of Reactor Materials with Contaminants Outgassed from Graphite," p 698 in the Proceedings of the US/UK Meeting on the Compatibility Problems of Gas-Cooled Reactors Held at Oak Ridge National Laboratory, February 24–26, 1960, TID-7597 (March 3, 1961).

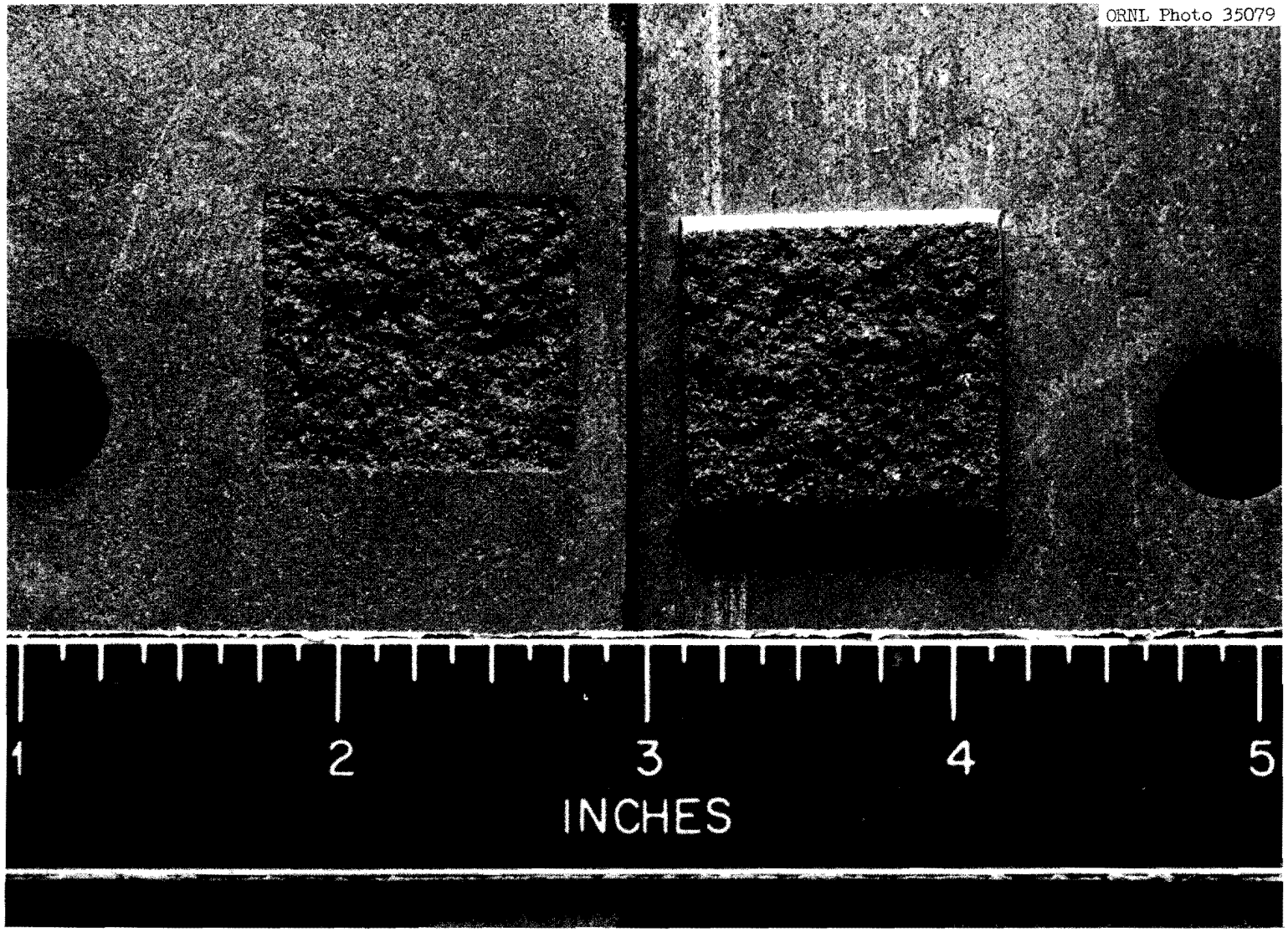

Fig. 1. Sample of Type 304 Stainless Steel Bonded to Graphite During Exposure in Impure Helium at 760°C.

EQUIPMENT AND PROCEDURE

The test equipment shown in Fig. 2 is composed of a two-piece cylinder whose halves can be joined in a vacuum-tight seal by use of a Conoseal assembly. A pneumatically actuated shaft passes through an O-ring seal in the upper half of the cylinder to provide the required force for pressing the specimens together during test. A vacuum system capable of keeping pressure below 5×10^{-6} mm Hg is joined to the cylinder by a flanged joint containing an O-ring seal. All tests performed have operated in the range of 1 to 5×10^{-6} mm Hg, as measured with an ion tube.

The system is heated by an electric furnace controlled by a Leeds & Northrup DAT controller-recorder capable of maintaining temperatures accurately to ±3°C. Controlling and recording thermocouples are brought into the cylinder through a Conax fitting and are placed in holes provided in the graphite disks, as shown in Fig. 3. The specimens shown in Fig. 3 consist of three different sizes to yield three different stress levels in each test.

A typical test is performed in the following manner. Specimens are degreased with acetone and placed in the bottom half of the test cylinder. The top half containing the shaft is put in place, and the Conoseal joint is fastened. After the cylinder is leak-checked to establish that the system is vacuum-tight, it is fastened to the pneumatic loading unit and to the vacuum system. The entire system is pumped down to approximately 5×10^{-6} mm Hg and held at this pressure for a minimum of 24 hr before heatup. The test area is then heated to test temperature, usually in about 2 1/2 hr. During heating the pressure in the system may increase to about 5×10^{-4} mm Hg; however, it is reduced to 5×10^{-6} within about 24 hr. Once operating temperature is reached, the load is applied to the specimens by the pneumatically actuated shaft.

After 1000 hr at temperature, the load is released and the furnace is shut down. The system is kept under vacuum until the cylinder has cooled to room temperature, which usually takes about 24 hr. The

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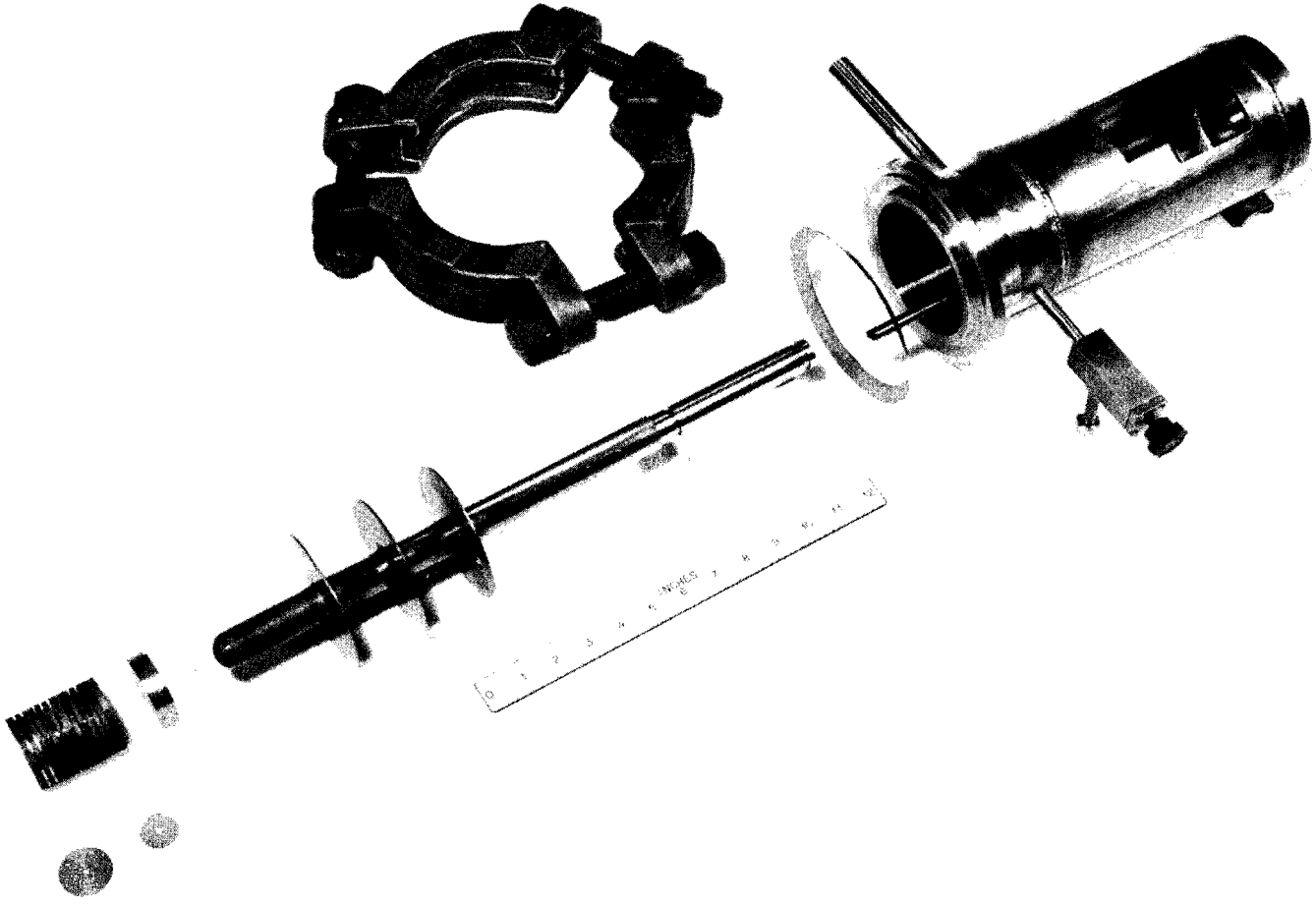

Fig. 2. Unassembled Parts of Apparatus Used for Contact Carburization Tests.

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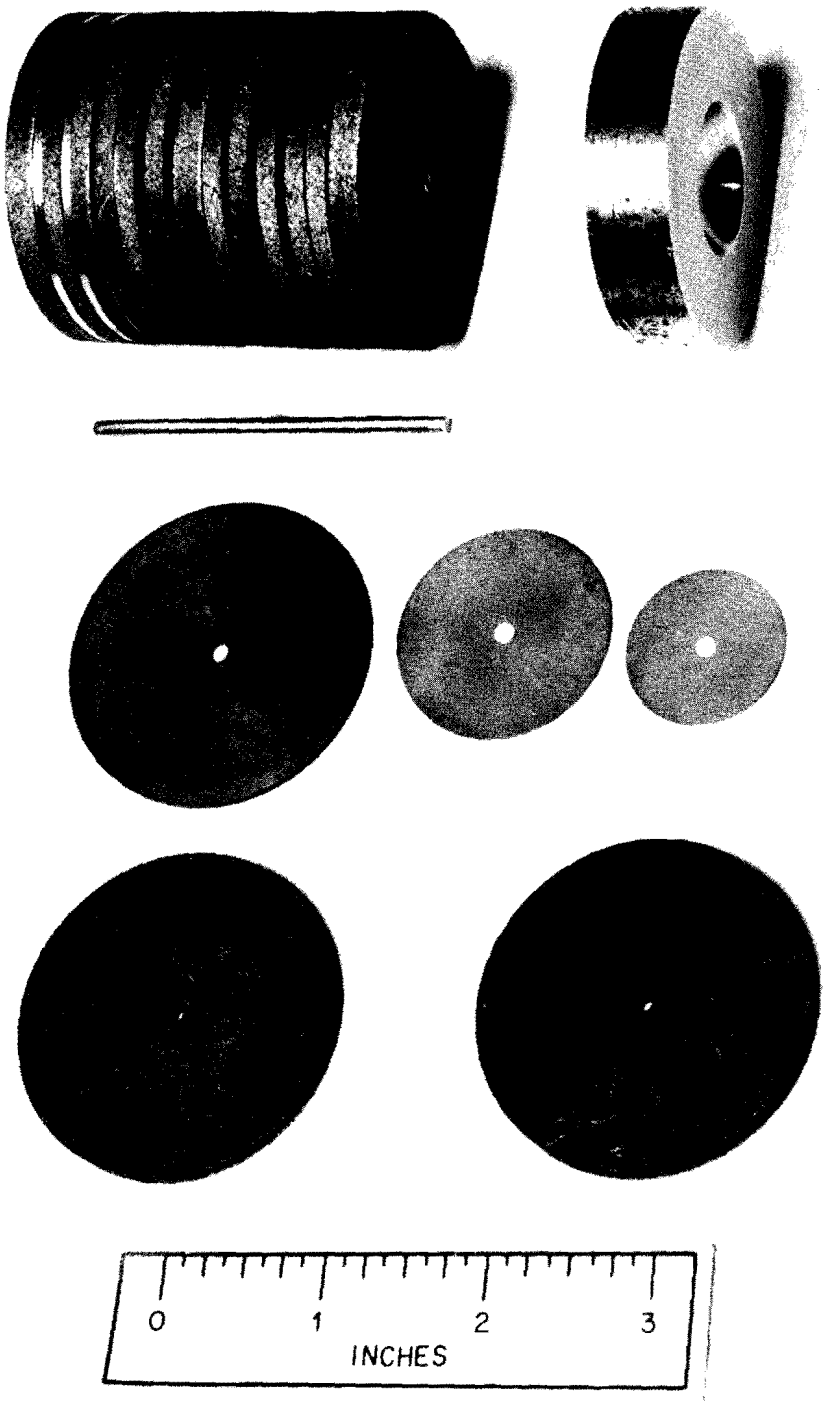


Fig. 3. Relative Size of Specimens and Assembled Stack of Specimens as Used in Contact Carburization Tests.

specimens are then removed and examined visually before being subjected to such destructive tests as metallographic examination, hardness testing, and chemical and x-ray diffraction analyses.

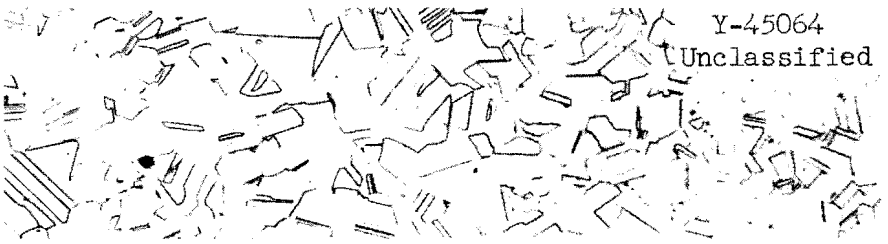
MATERIALS

Type 304L stainless steel sheet of two thicknesses from two different heats have been used in this investigation. The chemical composition of each heat is shown in Table 1, and a representative microstructure of each thickness of sheet in the fully annealed condition is shown in Fig. 4. In the first three tests, at 705, 650, and 540°C, respectively, some specimen surfaces were preoxidized, copper-plated, or electropolished after bright annealing in dry hydrogen. The copper layer on all plated specimens was 0.005 in. thick. Preoxidized specimens were produced by heating in air to 925°C for 4 hr.

Table 1. Chemical Composition of Test Materials

Element	Content (%)	
	0.005-in. Sheet	0.063-in. Sheet
C	0.025	0.027
Cr	17.28	18.32
Ni	10.50	10.36
Si	0.62	0.51
Mn	1.53	1.53
P	0.018	0.024
S	0.008	0.017
Fe	69.47	67.62

(a)



(b)

Fig. 4. Representative Microstructures of As-Received Type 304L Stainless Steel Used in Tests Showing (a) Inclusions Present in 0.063-in. Sheet and (b) Complete Thickness of 0.005-in. Sheet. Etchant: aqua regia. 250X.

RESULTS AND DISCUSSION

Test runs at 650 and 705°C for 1000 hr, under apparent contact pressures of 500, 1000, and 2000 psi, produced extensive bonding and carburization of all untreated surfaces of type 304 stainless steel specimens. Copper-plated and preoxidized surfaces were unaffected. Photomicrographs of a typical area of a 0.063- and 0.005-in.-thick specimen are shown in Figs. 5 and 6, respectively. Carburization of the 0.063-in. specimens at 705°C extended to a depth of approximately 0.030 in., which compares favorably with the value of 0.022 in. calculated by Anderson and Sneesby[4] for type 304 stainless steel exposed to carbon-saturated liquid sodium for 1000 hr at the same temperature.

The 0.005-in.-thick specimens were severely embrittled, showing virtually no ductility in bend tests. The carbon content of the 0.005-in. specimen under an apparent contact pressure of 2000 psi at 705°C was 3.59%, again comparing favorably with the values of 3.2 and 3.4% at 705°C reported by Anderson and Sneesby in their work with sodium. Rockwell hardness values on the thin specimen ran as high as R_C48. X-ray analysis of the bulk metal specimen, in contrast to the previous work with sodium, revealed the presence of $Cr_{23}C_6$, Ni, and type 304 stainless steel. The phase appearing at the graphite-metal interface was identified as Cr_7C_3, but the compounds Cr_3C_2 and Fe_3C were not detected.

At 540°C, under apparent contact pressures of 500, 1000, and 2000 psi, no bonding or detectable carburization occurred, and the ductility of thin specimens was unaffected. Two tests at 595°C, however, gave inconclusive results. In one test, where the contact pressure was the same as that previously employed, partial bonding and carburization occurred, but only on certain specimens and to a lesser extent than in the tests at higher temperature. The hardness of thin specimens in the area where bonding occurred was as high as R_C55. In the other test, where the apparent contact pressures were 1200, 2400, and 5100 psi, no bonding and only spotty carburization were observed, as shown in Figs. 7 and 8. These anomalous results are ascribed to the nonuniform load distribution which existed in the first test and to the fact that 595°C is the approximate

Fig. 5. Carburization and Bonding of 0.063-in.-Thick Specimen of Type 304L Stainless Steel in Contact with Graphite for 1000 hr at 705°C. Etchant: picric acid.

Fig. 6. Microstructure of 0.005-in.-Thick Specimen of Stainless Steel Carburized in Contact with Graphite for 1000 hr at 705°C. Etchant: aqua regia.

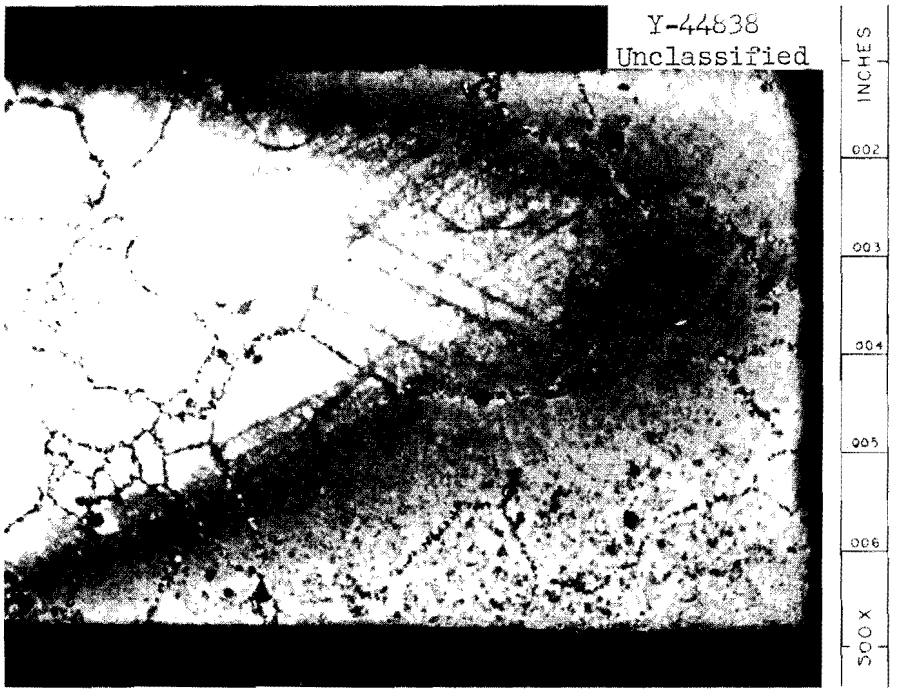


Fig. 7. Extensive Carburization Produced Locally in 0.005-in.-Thick Stainless Steel Sheet Exposed to Graphite at High Contact Pressures for 1000 hr at 595°C. Etchant: 2% Nital.

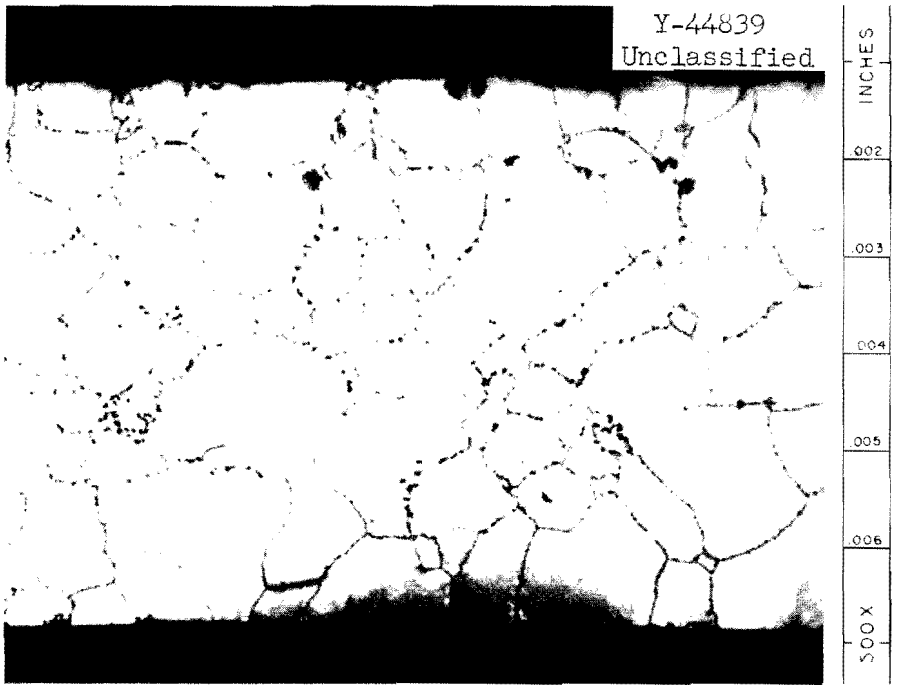


Fig. 8. Stainless Steel Sheet 0.005-in.-Thick After Exposure to Graphite at High Contact Pressures for 1000 hr at 595°C. Lack of bonding or significant reaction with graphite can be noted. Etchant: 2% Nital.

threshold temperature for the reaction of stainless steel with graphite under contact pressure (in the absence of significant amounts of gases).

Control specimens not in contact with graphite were included in tests at all temperatures. These specimens did not show detectable carburization, as seen in Fig. 9, which is a typical microstructure of a control specimen. For comparison the microstructure of bright-annealed material prior to testing is shown in Fig. 4. These results provide evidence that gaseous impurities existing in the evacuated system did not play a significant role in the carburizing reaction.

More evidence to support this conclusion, which is also consistent with the data reported by Giacobbe,[1] is provided by the existence of such interfacial areas as that shown in Fig. 10 of a portion of a specimen carburized at 705°C. It is apparent that carburization occurred only through areas where graphite was in intimate contact with the metal. Areas in the metal that were adjacent to voids in the graphite contained considerably less carbon than areas of the metal in intimate contact with graphite.

As a result of nonuniform loading conditions a quantitative relation between contact pressure and extent of carburization was not established in these tests, but a qualitative relationship was demonstrated by carburization gradients existing in individual specimens. Figure 11 is a typical example. The carburization gradient is believed to reflect the stress gradient which existed across the face of the specimen.

SUMMARY

Tests performed to date reveal that solid-state reactions resulting in carburization of type 304 stainless steel occur at temperatures as low as 595°C when graphite and type 304 stainless steel are held in intimate contact. The role of gaseous impurities existing at pressures of 10^{-6} mm Hg is insignificant in the process of carburization. Since carburization is closely associated with intimate contact between graphite and metal, it is apparent that external forces serving

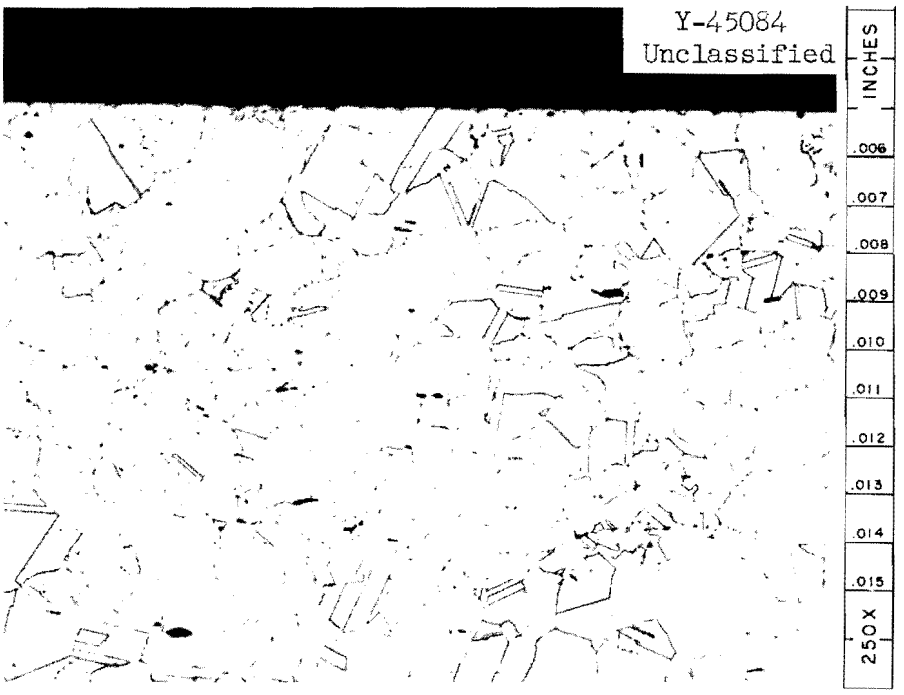


Fig. 9. Microstructure of Stainless Steel Control Specimen Not in Contact with Graphite. Note similarity to as-received material shown in Fig. 4(a). Etchant: aqua regia.

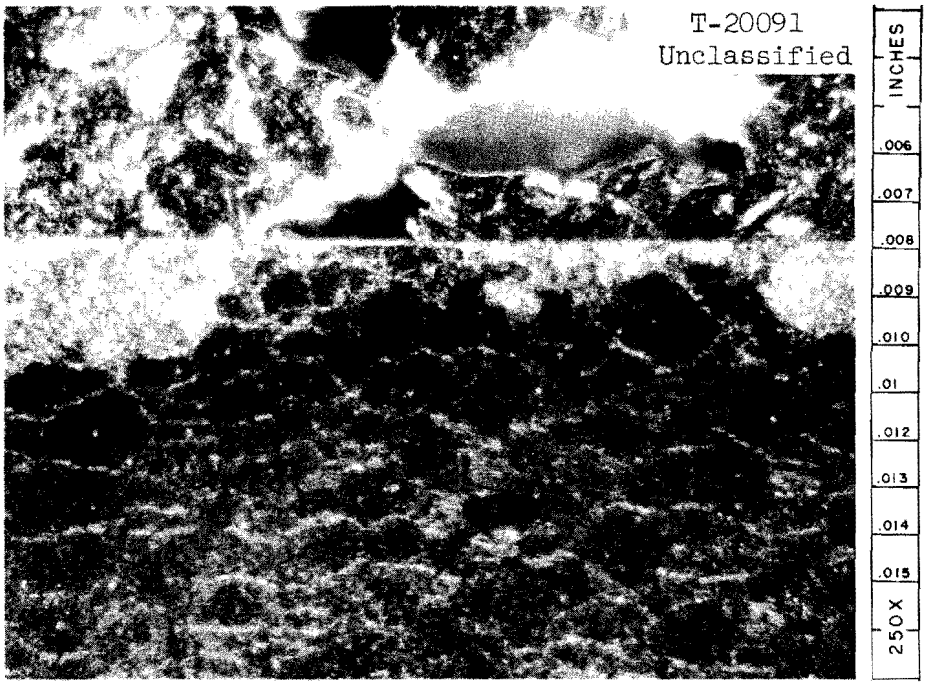


Fig. 10. Interface Region of Specimen Tested for 1000 hr at 705°C. Reaction with the graphite is much greater in areas of the specimen that are in intimate contact with graphite. Dark-field illumination, as-polished.

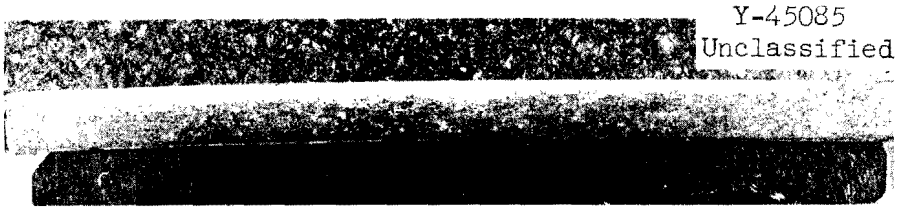


Fig. 11. Gradation of Carburized Layer Along Radius of 0.063-in.-Thick Stainless Steel Specimen. The carburized layer, which appears white under the oblique light, gradually decreases in thickness and disappears as one proceeds outward along the radius. Oblique lighting. Etchant: aqua regia. 5X.

to bring more graphite into contact will cause a greater degree of carburization. This has been demonstrated qualitatively in individual specimens where carburization gradients have reflected stress gradients resulting from nonuniform loading.

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