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EFFECT OF ENVIRONMENT ON THE CREEP PROPERTIES OF TYPE 304 STAINLESS STEEL AT ELEVATED TEMPERATURES

H. E. McCoy, Jr.
D. A. Douglas, Jr.

OAK RIDGE NATIONAL LABORATORY
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ORNL-2972

Contract No. W-7405-eng-26

Metals and Ceramics Division

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DATE ISSUED

SEP 5 1962

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ABSTRACT

Many of the components in the Experimental Gas-Cooled Reactor will be made up of type 304 stainless steel. Among the more critical of these items are the thin-walled capsules which serve to hold the uranium dioxide fuel and to contain the gaseous fission products. In order to make an accurate estimate of the life of these capsules, an extensive test program is being conducted to evaluate the influence of the service environment. Since the composition of the environment of the reactor will vary during service, the approach taken in this study was that of evaluating the influence of each impurity gas in its pure form. The environments studied include Ar, H_2, CO, CO_2, N_2, air, and O_2.

The results of tests which have been completed indicate that air, CO, CO_2, and N_2 are strengthening to this alloy. Carburization and nitriding are believed to be primarily responsible for the strengthening in these environments. At 1500°F, O_2 at 1 atm pressure has a deleterious effect on the creep properties, but at 1700°F the creep properties are improved. Creep tests at 1500°F in various argon-oxygen mixtures show that small oxygen concentrations cause pronounced strengthening with a maximum effect being observed at 10 ppm O_2. At 1500°F the creep properties appear to be unaffected by hydrogen, but at 1700°F deleterious effects are observed. Tensile tests were used to evaluate the influence of carbon on the rupture ductility of this material. It was found that significant reduction in ductility occurred as the carbon content was increased. It was found that copper plating effectively reduced the rate of carburization at 1300°F. The service life of copper films at higher temperatures was seriously limited.

Several general remarks are made relative to conceivable compatibility problems during reactor operation associated with the type 304 stainless steel cladding. It is felt that the most serious problem is associated with carburization and the subsequent distribution of the carbon in the metal.

EFFECT OF ENVIRONMENT ON THE CREEP PROPERTIES OF TYPE 304 STAINLESS STEEL AT ELEVATED TEMPERATURES

INTRODUCTION

The creep behavior of materials has been studied by metallurgists from both the theoretical and applied viewpoints for many years. In general, these studies have been directed toward understanding the effects of metallurgical variables such as composition, grain size, and fabrication and the effects of service variables such as stress and temperature. In recent years it has become apparent that in certain cases one must be concerned with another variable; namely, the service environment. The problem is more widespread than is commonly recognized and a number of examples have been documented in the literature.[1]

In considering the problem of predicting the mechanical behavior of the fuel element capsules in the Experimental Gas-Cooled Reactor (EGCR), it was appreciated that the service environment was an important variable pertaining to the creep and rupture of the structural metal. Although the EGCR will be cooled by helium, significant quantities of other gases will result from the outgassing of the graphite moderator and the reaction between the graphite and inleakage of moist air and steam. Thus, it is expected that CO, CO_2, CH_4, H_2, N_2, O_2, and H_2O will be present in the coolant stream in small quantities which will vary throughout the operating life of the reactor. Because of the uncertainty of the composition of the gas in contact with the fuel element capsule, the approach taken to this problem has been to study the behavior of type 304 stainless steel in each of the gases cited above in its pure form. It is believed that data from these tests will reveal any compatibility problems which may exist in mixtures of these gases. Much of the testing program is now directed toward establishing

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[1]R. F. Hehemann and G. Mervin Ault (eds.), High Temperature Materials, pp 429–97, Wiley, New York, 1959.

the effects produced when an inert carrier is contaminated with a small partial pressure of one or more of these constituents. The fact that the metal capsules will operate over a temperature range from 1200 to 1700°F has increased the magnitude of the problem.

EXPERIMENTAL DETAILS

Test Specimens

Type 304 stainless steel in the form of 0.060-in. sheet was used in these studies. The chemical analyses of the heats used are given in Table 1. Heat C was the test material from which most of the results described herein were obtained. The material will not be specified unless a material other than heat C was used. The specimens had a gage width of 0.500 in. and a gage length of 4.00 in. Sheet specimens were chosen because of their large ratio of surface area to volume.

Table 1. Chemical Composition of Test Specimens in Weight Percent

Heat No.	Fe	Ni	Cr	Ti	Mo	Cb	Mn	Al	C	Si
B	69.08	9.54	18.19	0.015	0.24	< 0.2	1.47	0.11	0.042	0.51
C	69.74	9.53	17.60	0.18	0.23	< 0.2	1.33	0.03	0.033	0.51

Testing Apparatus

The environment surrounding specimens during creep-rupture tests was controlled by means of a test chamber similar to that shown in Fig. 1. The test chamber is a type 310 stainless steel tube about which is placed a Nichrome-wire heating element. The joint between the extension rod and the test chamber is made with U-cup pressure-vacuum seals. These seals make it possible to maintain vacuum or pressure within the test chamber and yet not cause significant resistance to movement of the extension rods. Water jackets are provided at both the top and bottom of the chamber to cool the seals. Openings in the top of the chamber allow entrance of four Chromel-Alumel thermocouples for measuring the temperature of the test specimen. Two of the thermocouples are made using standard insulators and are attached directly to the gage length of the specimen.

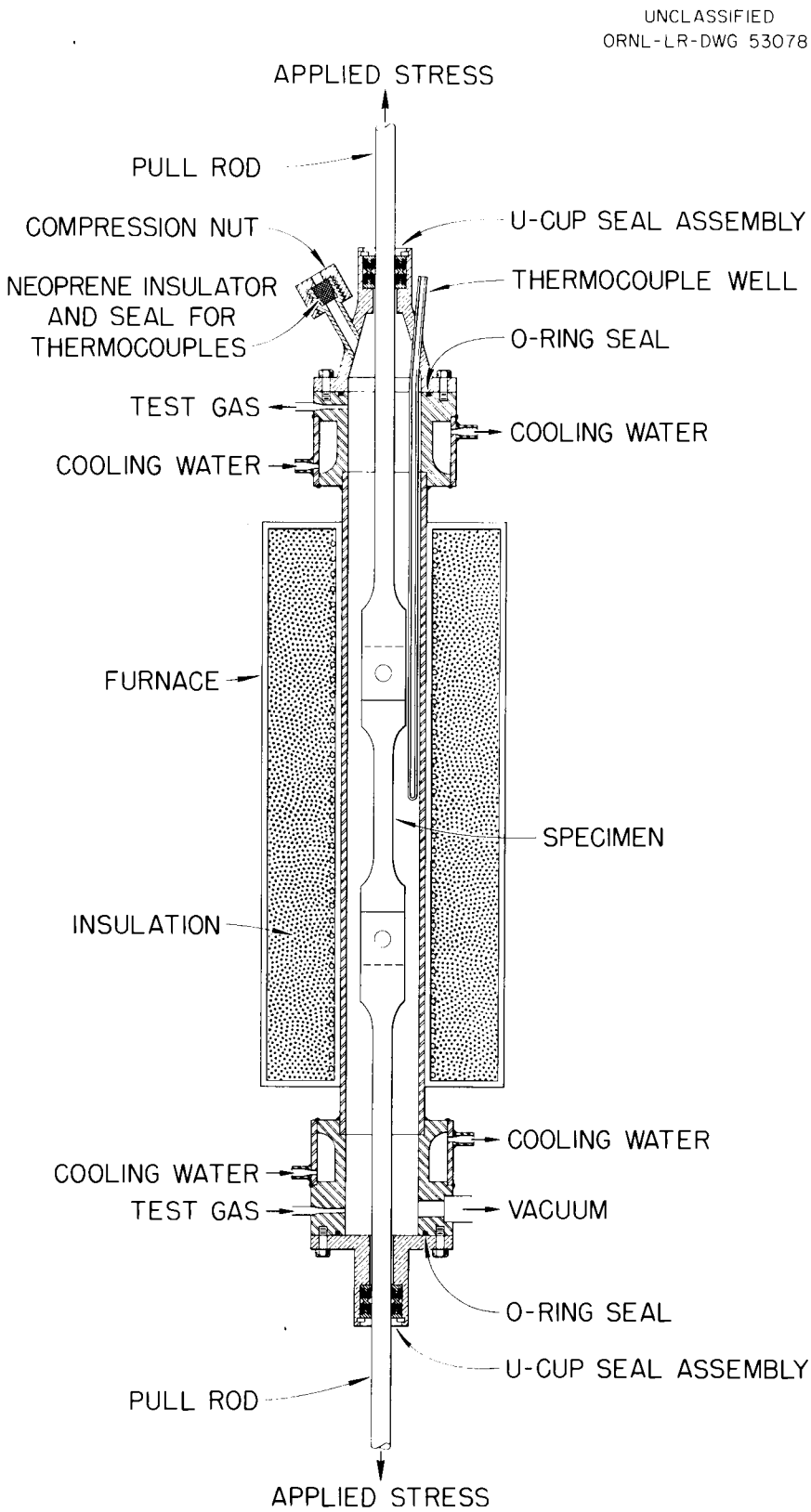

Fig. 1. Chamber for Environmental Stress-Rupture Tests at Elevated Temperatures.

The other two thermocouples are swaged assemblies consisting of Chromel-Alumel wires, MgO insulation, and Inconel sheathing. The latter two thermocouples are placed at the same horizontal positions in the chamber as the other thermocouples, but their exact distances from the specimen are not known.

Air tests were run in a furnace of the type shown in Fig. 1, but without the inner protective chamber. Temperature measurements were made with Chromel-Alumel thermocouples attached directly to the specimen.

Experimental Procedure

To minimize the effects which a particular environment may have upon the properties of a specimen by exposure before the stress is applied, all tests except those run in air were heated to the test temperature under a vacuum of less than 1 μ. When a nonoxidizing environment was desired, the chamber was brought to temperature with a vacuum of less than 0.1 μ. After the test temperature was reached, the test environment was admitted and the load applied. Tests in CO, CO_2, N_2, H_2, and O_2 were run in flowing environments since these gases react with the chamber walls and the specimen. Sufficient flow rates were used to ensure an ample supply of gas to the specimen. These gases were dried before being introduced into the test chamber. Tests in an argon environment were run under static conditions. Although high-purity argon was used, thin oxide films were formed after exposure to this gas for several hundred hours. Zirconium strips were suspended near the test specimen to act as a getter in purifying the test environment. After the test temperature was reached, the test chamber was charged with argon to about 5 psig and the gas supply shut off.

The initial temperature distribution across the test section of the specimen is determined by the two thermocouples attached to the specimen. However, many of the test environments used react with Chromel-Alumel thermocouples and alter their temperature-emf characteristics. Hence, the swaged thermocouples are used for controlling the furnace temperature. The control point is adjusted so that the test section achieves the proper temperature. Thus the effect of test environment on thermocouple properties is not a variable in this testing procedure.

RESULTS

Creep Tests

The results of creep-rupture tests in Ar, CO, CO_2, H_2, N_2, O_2, and air are given in Figs. 2, 3, and 4 for conditions where sufficient tests have been run at equivalent temperatures and stresses to compare the effects of environment. In most cases, each curve plotted represents the results of at least two tests. The creep behavior noted in argon is used as the reference with which the properties in other environments are compared.

The results indicate that for the test conditions examined, the various test environments influence the creep properties in the following ways:

1. Environments of air or nitrogen decrease the creep rate at 1500 and 1700°F.

2. Strengthening is observed in CO and CO_2 at 1500 and 1700°F.

3. At 1500°F the creep properties are essentially equivalent in argon and hydrogen.

4. At 1700°F the creep life is less in hydrogen than in argon.

5. The creep strength is less in an oxygen environment at 1500°F than in an argon environment.

6. At 1700°F strengthening is observed in an oxygen environment.

The specimens were examined visually after each test was terminated. Representative results are given in Table 2.

Table 2. Macroscopic Examination of Creep Specimens

Environment	Temperature (°F)	Surface Characteristics
CO	1300–1500	Sooty, dark adherent oxide, slightly magnetic
CO_2	1500	Dark scaly oxide, magnetic
Air	1300	Dark adherent oxide, slightly magnetic
Air	1500–1700	Dark scaly oxide, strongly magnetic
O_2	1500–1700	Dark scaly oxide, strongly magnetic
Ar, H_2	1300–1700	Bright, nonmagnetic

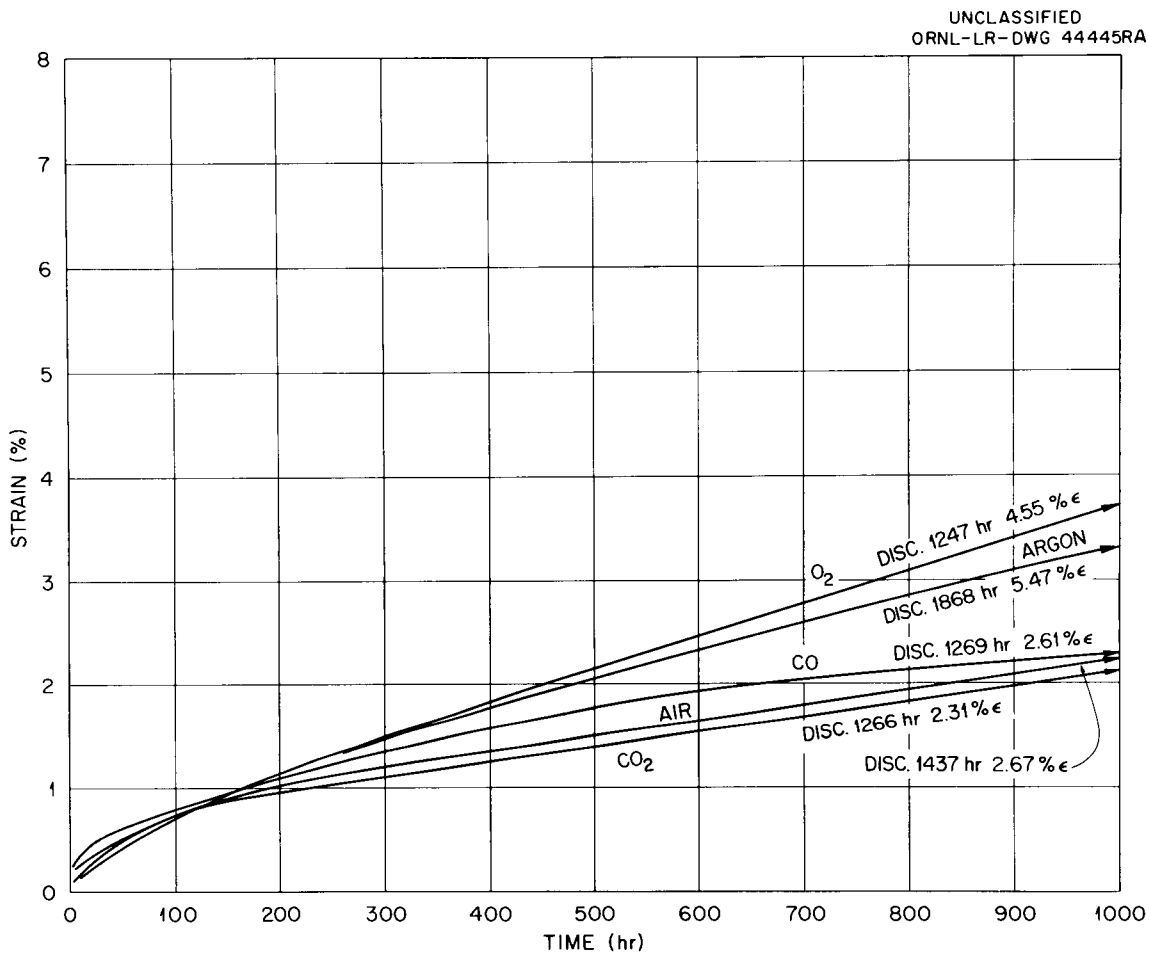

Fig. 2. Effect of Environment on the Creep Properties of Type 304 Stainless Steel at 1500°F and 3000 psi.

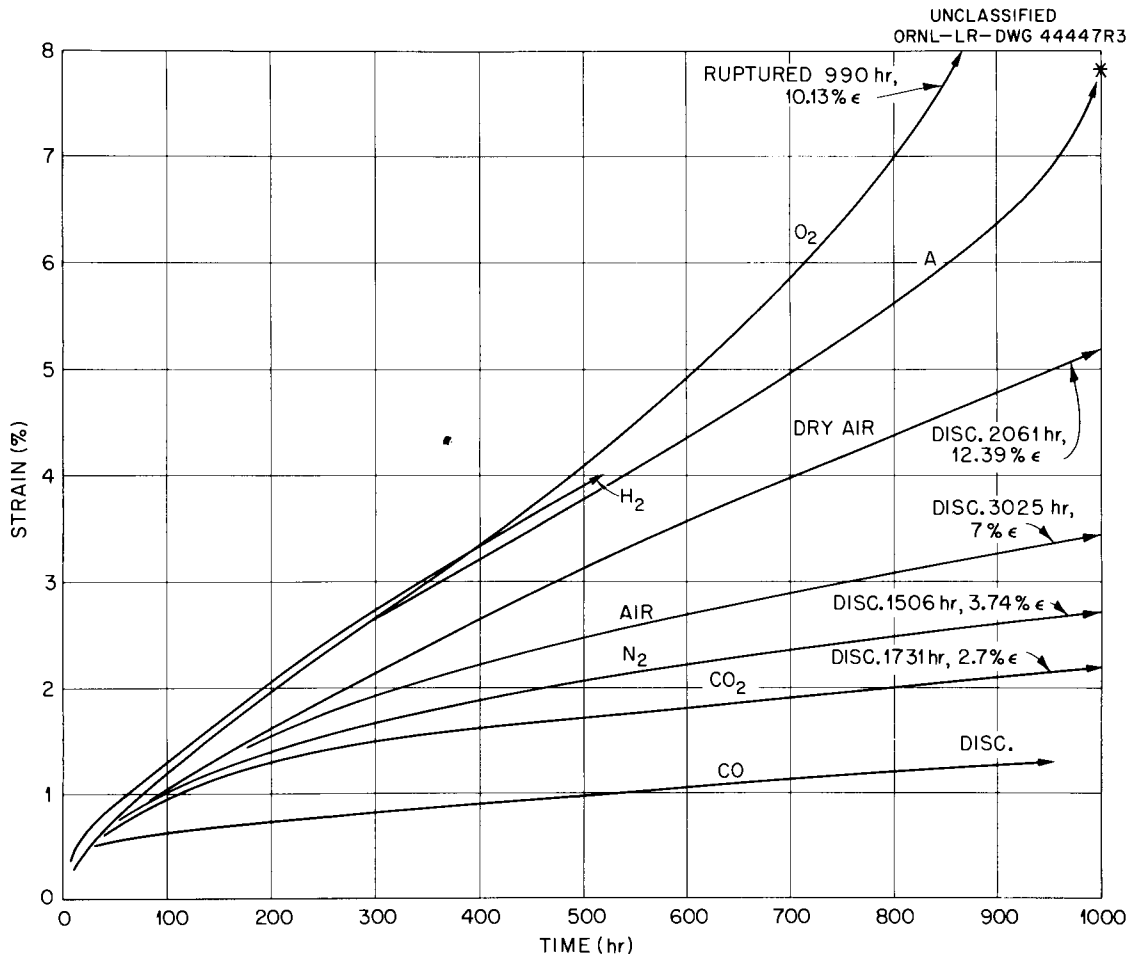

Fig. 3. Effect of Environment on the Creep Properties of Type 304 Stainless Steel at 1500°F and 3400 psi.

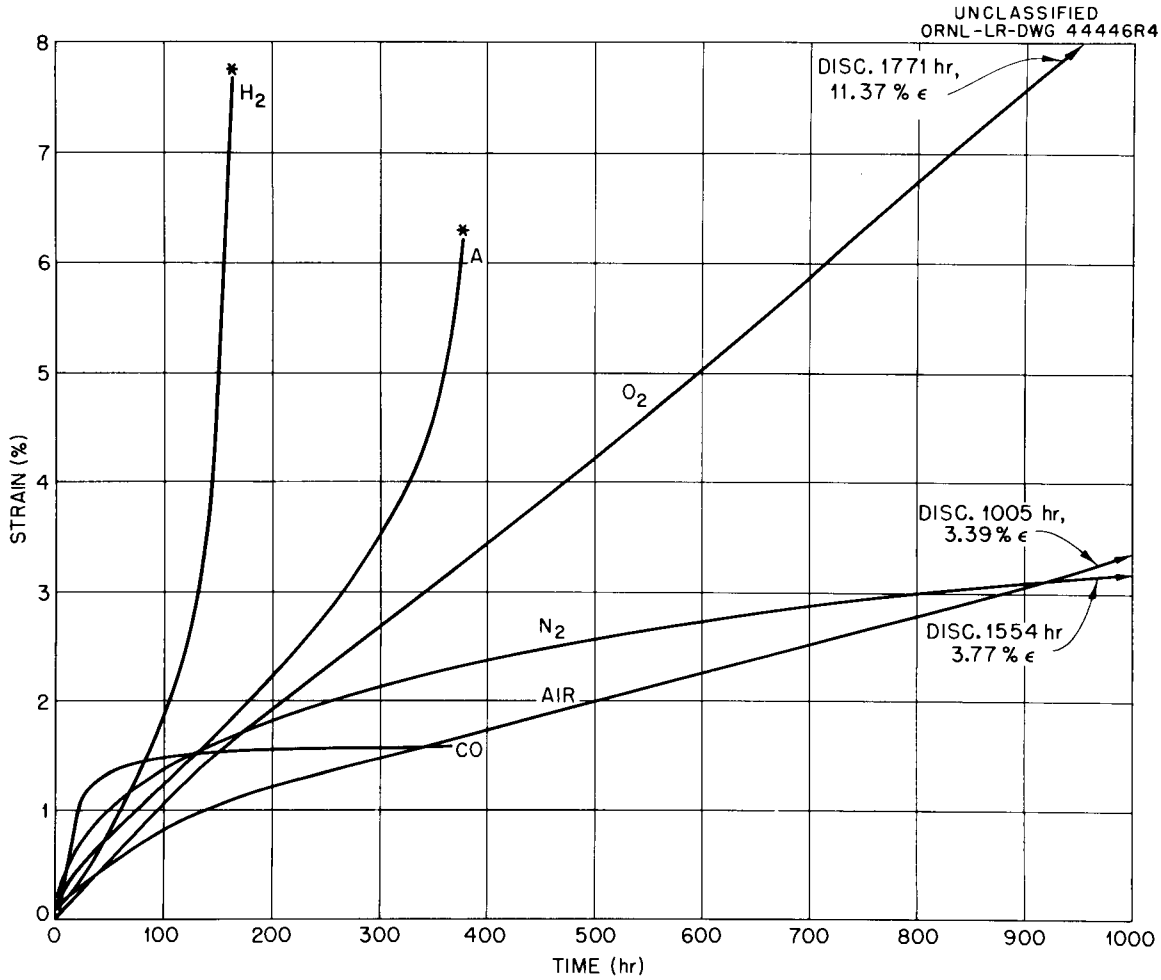

Fig. 4. Effect of Environment on the Creep Properties of Type 304 Stainless Steel at 1700°F and 1200 psi.

The observed reduction of strength at 1500°F in oxygen was somewhat unexpected. In an effort to more fully evaluate the influence of oxygen on the creep properties of type 304 stainless steel, a series of creep tests were run in various argon-oxygen mixtures. The results of these tests are summarized in Figs. 5, 6, and 7. The oxygen-argon mixtures were prepared in standard gas cylinders and a flow rate through the test chamber of approximately 0.1 cfh was used. The relatively large effects of small partial pressures of oxygen on the creep strength probably accounts for the difficulties encountered in reproducing test results in an argon environment. The crack-density plot shown in Fig. 7 was determined metallographically.

Metallographic Examination of Creep Specimens

Several of the test specimens were examined metallographically. A series of representative photomicrographs are given. Figures 8 and 9 illustrate the type of microstructure which results from testing in argon and hydrogen at temperatures between 1300 and 1700°F with the exception of some variation in grain size. Note the steps on the surface which result from grain-boundary sliding and rotation of the grains. These steps were not observed unless the surface of the specimen was completely free of oxide.

Figure 10 is a photomicrograph of the gage section of a specimen tested at 3400 psi in air at 1500°F for 3025 hr. Features of importance are the surface oxide, the surface and internal cracks which follow grain boundaries, and the precipitate which is present. Several specimens tested at various stresses in air at 1700°F were examined. The test data relevant to this series are given in Table 3. Representative

Table 3. Creep-Rupture Tests in Air at 1700°F

Stress (psi)	Duration of Test (hr)	Reason for Termination	Strain (%)	Nitride Precipitate
1000	524	Discontinued	1.16	No
1200	1005	Discontinued	3.13	No
1200	1895	Discontinued	7.81	No
1500	726	Ruptured	10.88	Yes
2500	52.5	Ruptured	9.03	Yes

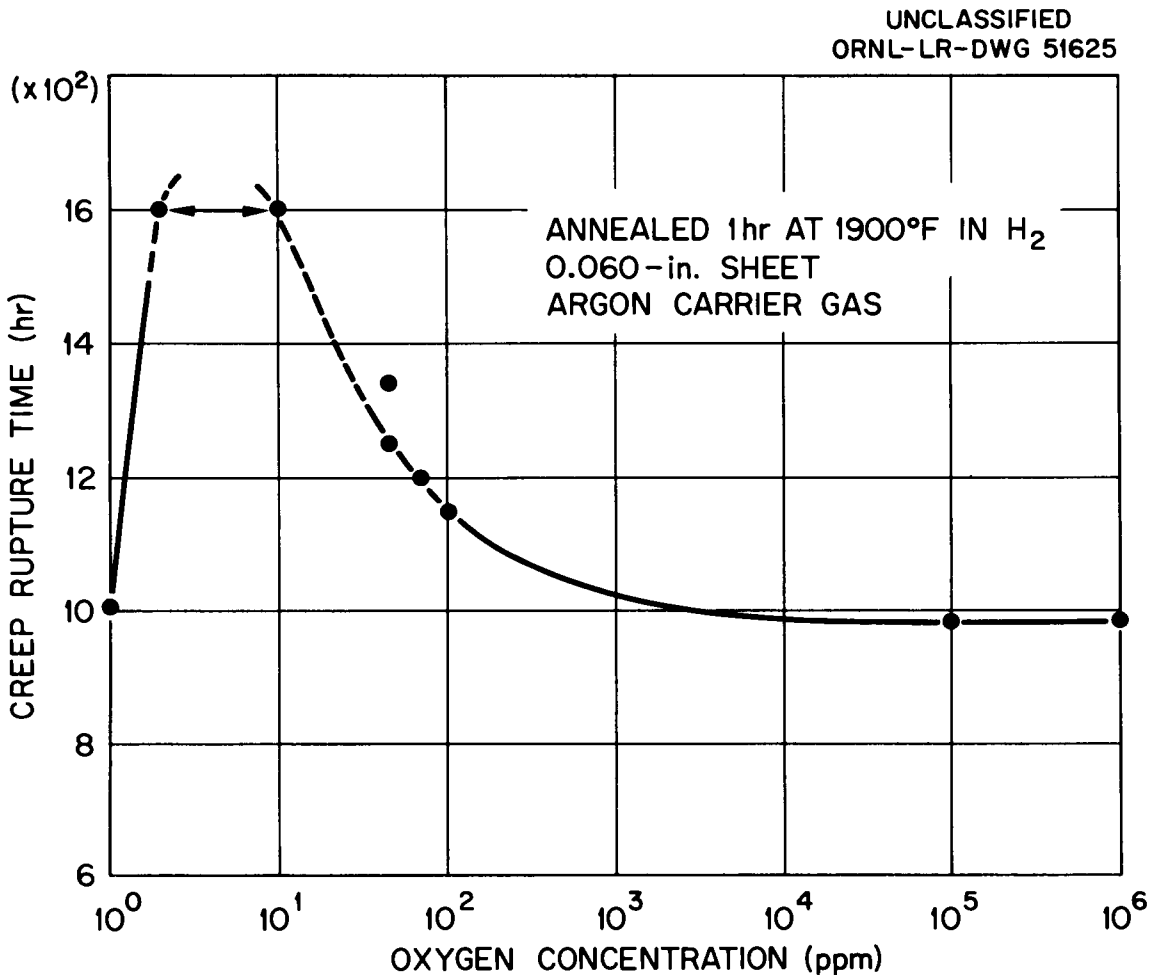

Fig. 5. Effect of Oxygen Concentration on the Rupture Life of Type 304 Stainless Steel at 1500°F and 3400 psi.

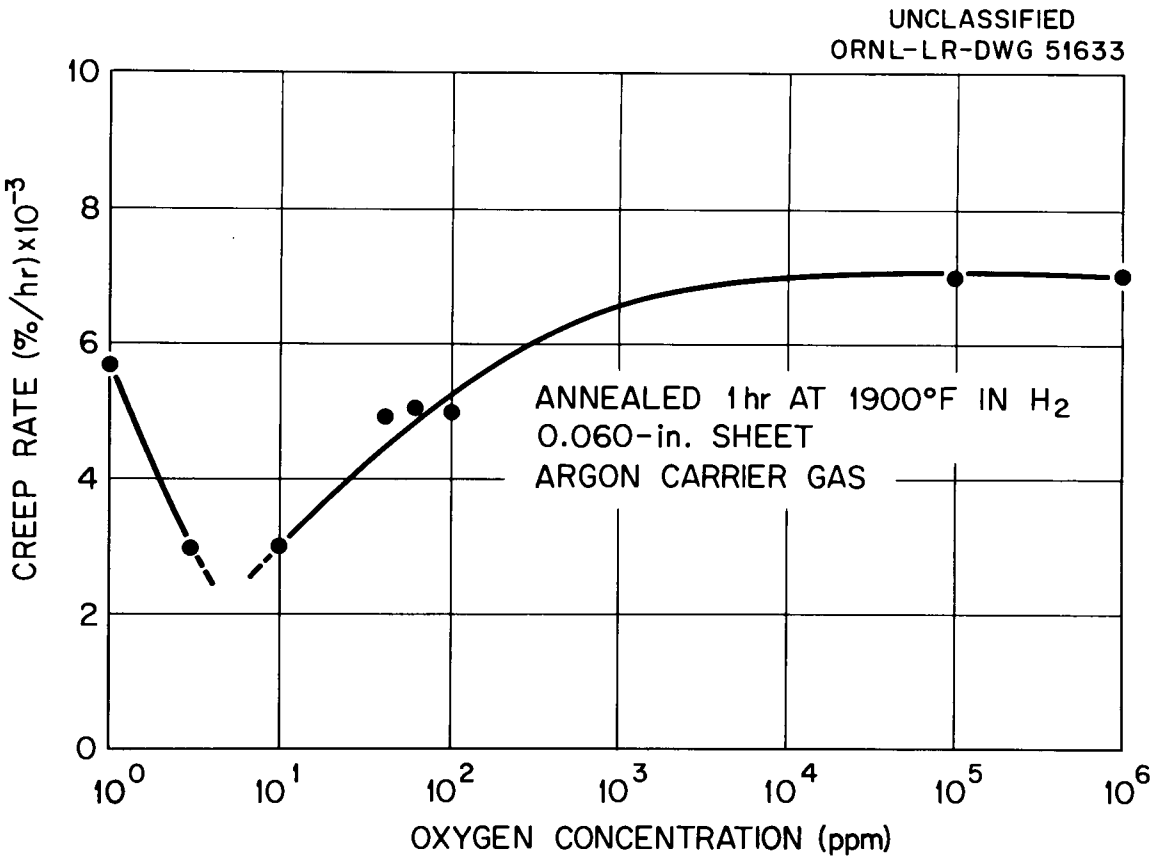

Fig. 6. Effect of Oxygen Concentration on the Creep Rate of Type 304 Stainless Steel at 3400 psi and 1500°F.

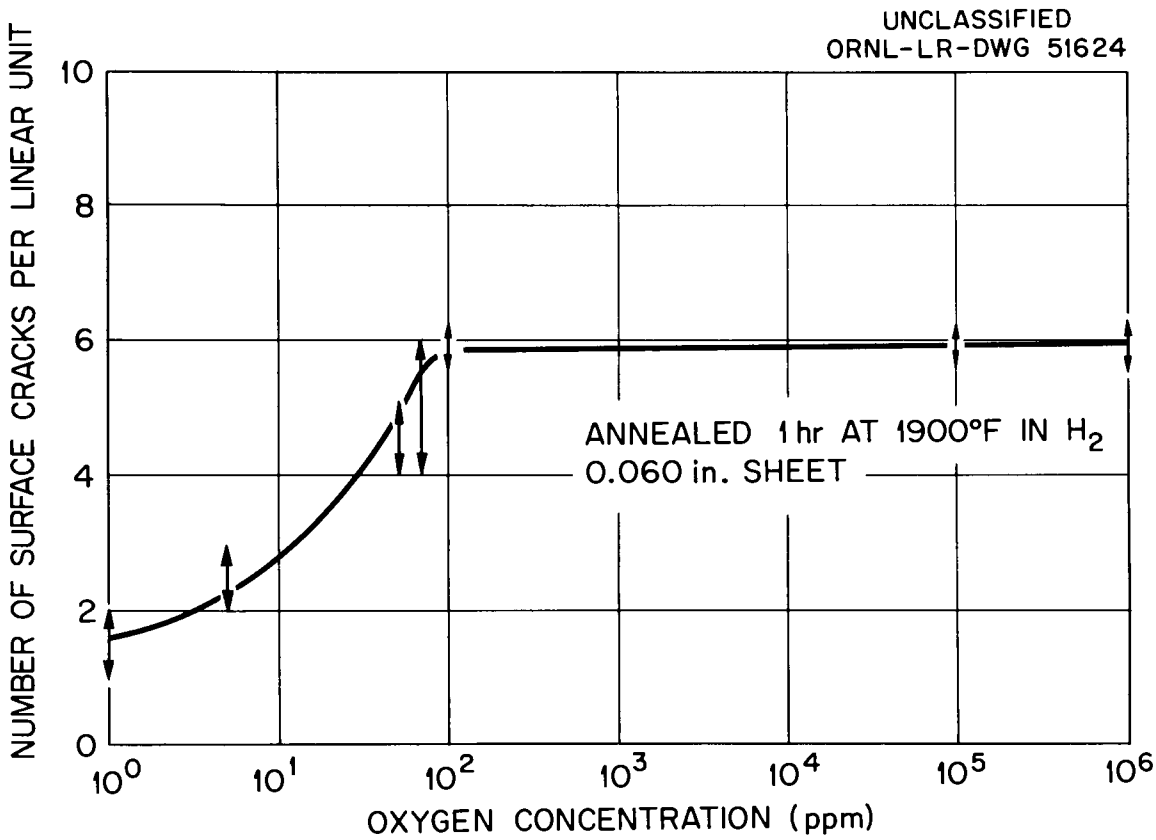

Fig. 7. Surface Crack Density of Type 304 Stainless Steel in Argon-Oxygen Environments Stressed in Tension at 3400 psi and 1500°F.

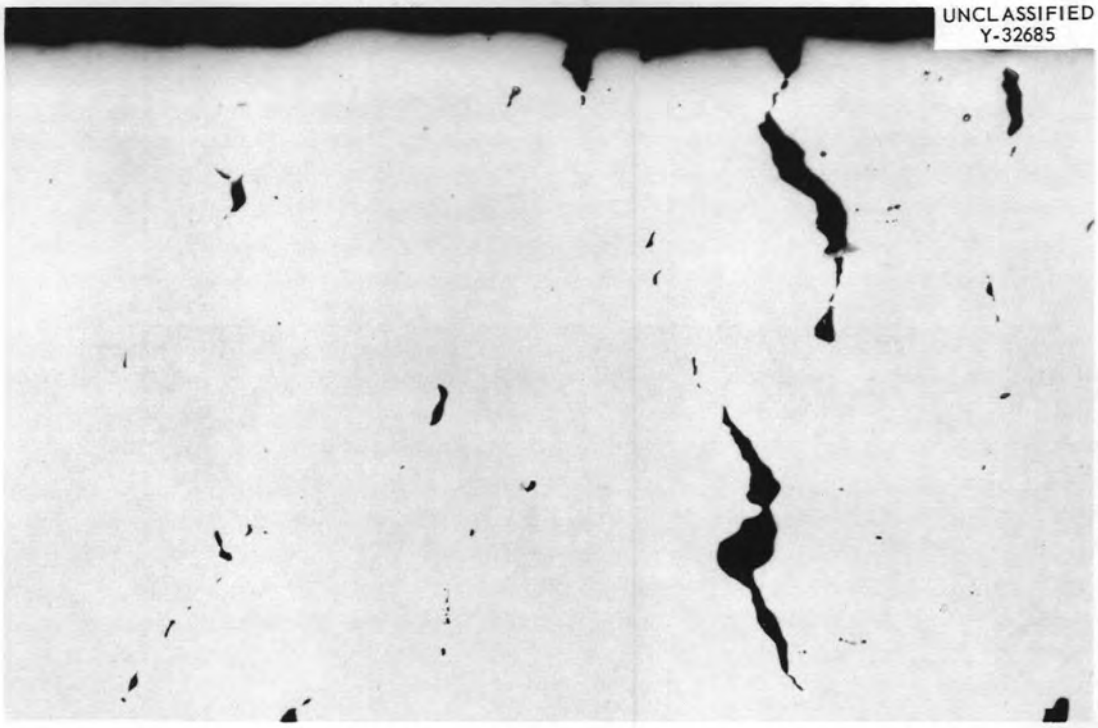

Fig. 8. Specimen Tested in Hydrogen at 1700°F and 1200 psi. Rupture Life: 161 hr. Unetched. 200X.

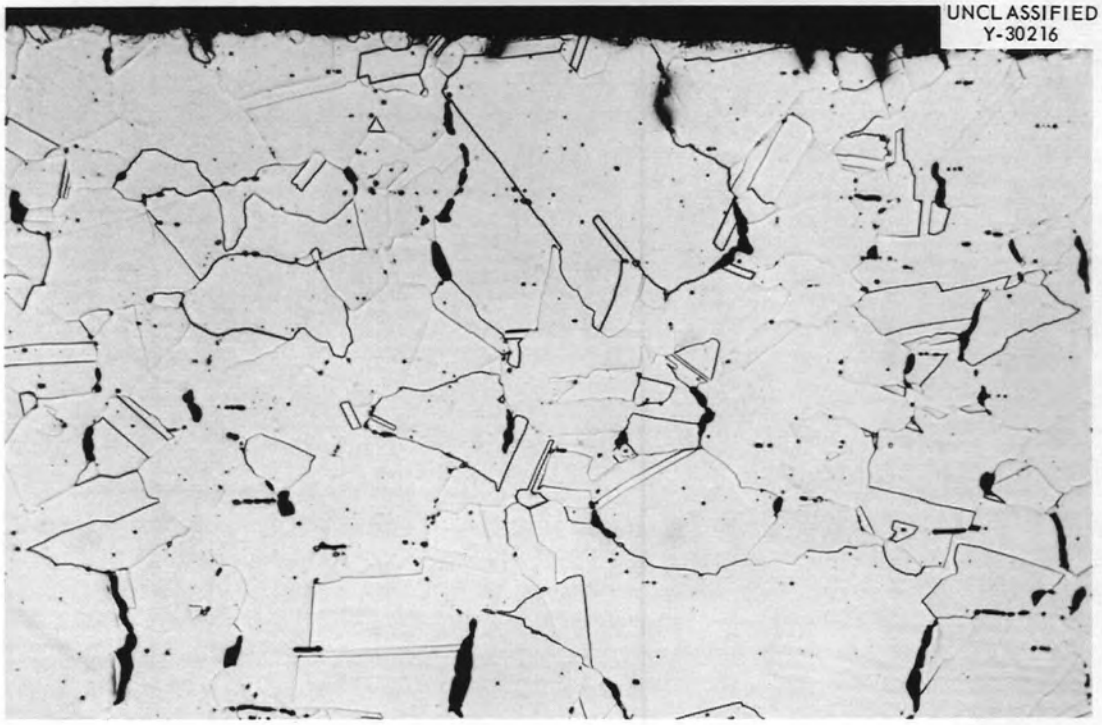

Fig. 9. Specimen Tested in Argon at 1500°F and 3400 psi. Rupture Life: 1000 hr. Etchant: Glyceria regia. 200X.

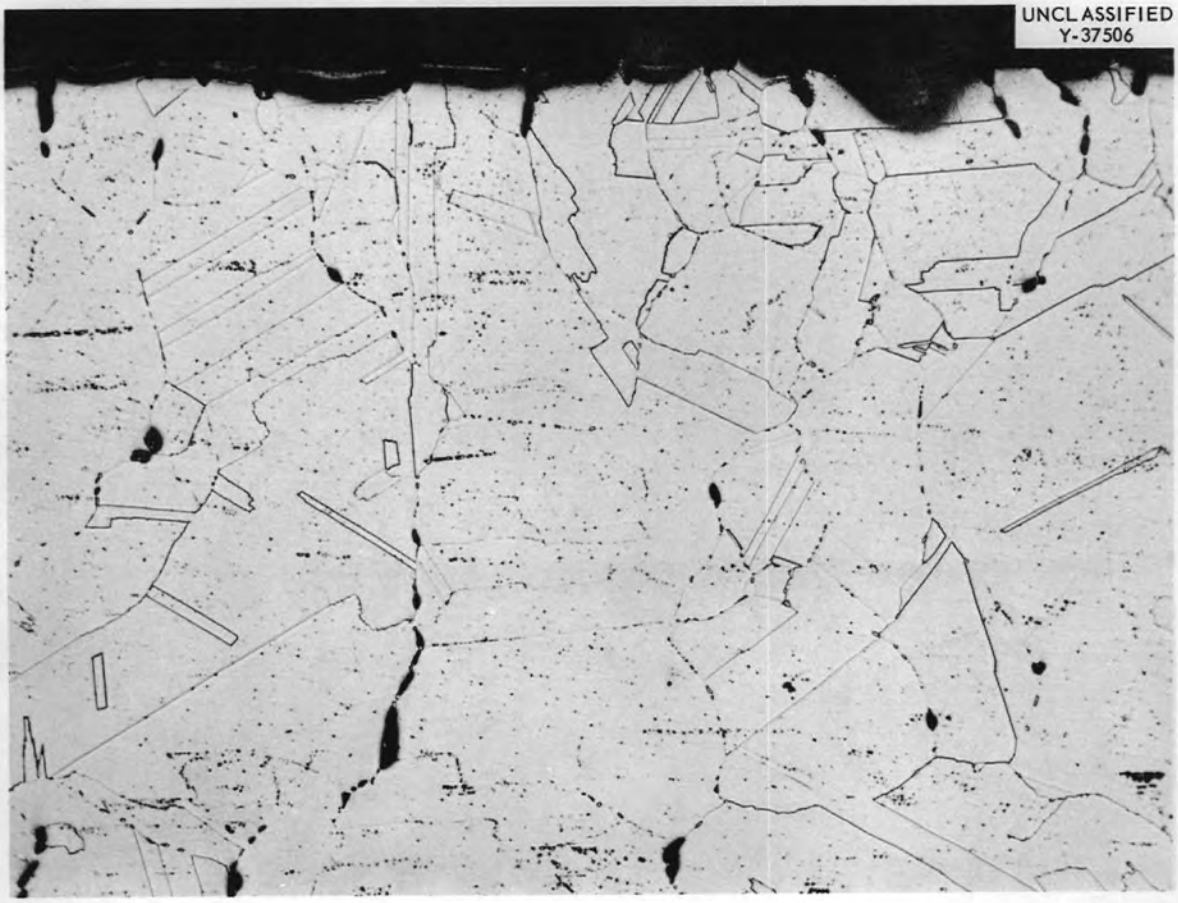

Fig. 10. Type 304 Stainless Steel Tested at 3400 psi in Air at 1500°F. Discontinued after 3025 hr of testing with 7.0% strain. Specimen etched with aqua regia. 200X.

photomicrographs are shown in Figs. 11–15. Note that a precipitate is present only in the last two photographs. Although the other photographs were made with the specimen in the as-polished condition, this does not account for the absence of the precipitate since etching has been observed to accent the precipitate only slightly. It is obvious that strain rate is an important factor in the formation of the precipitate in air at 1700°F. The role of total test time is felt to be important, although definitive experiments have not been run. Figure 16 also illustrates the importance of strain rate. Heavy precipitation occurred along the gage section with a very abrupt decrease in amount as the cross-sectional area increased. This general precipitate, as evidenced by the photomicrograph in the upper left-hand corner of Fig. 16, is actually composed of two precipitates, one lamellar in nature and the other of Widmanstätten geometry. The selective etching technique of Dulis and Smith[2] was used in which the matrix in the surface layer of the specimen was dissolved by prolonged attack in an alcoholic solution of picric and hydrochloric acids. The diffraction pattern of the surface was obtained with a recording spectrometer and the diffraction lines indicate the presence of CrN and Cr_2N.

Specimens tested in nitrogen at 1500 and 1700°F also exhibited heavy nitride formation. Figure 17 is a composite of photographs of a specimen tested at 3500 psi in nitrogen at 1500°F. The precipitate has been identified by x-ray diffraction as CrN and Cr_2N. Again note that the precipitate was formed only in the stressed portion of the specimen. The photomicrograph in the lower left-hand corner of Fig. 17 was taken of a portion of the specimen where the stress was very low during the test and is completely void of nitride formation. In the other photomicrographs of the gage section of the specimen, the density of precipitate is much greater in areas where extensive deformation has occurred. As illustrated by Fig. 18, a similar type of structure is observed in specimens tested in nitrogen at 1700°E. However, the precipitate forms more rapidly, is more generally distributed, and is much coarser.

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[2]E. J. Dulis and G. V. Smith, Trans. Met. Soc. AIME 194, 1083 (1952).

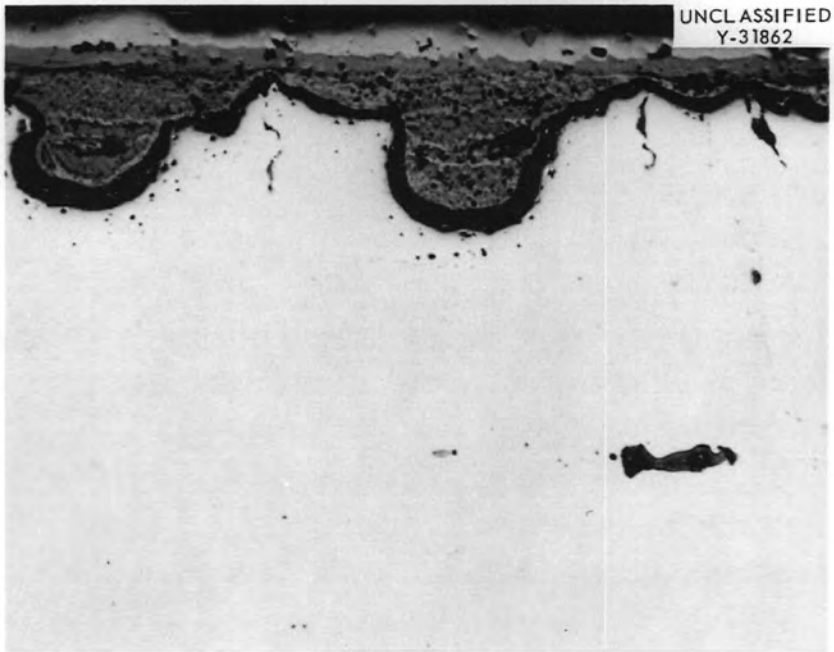

Fig. 11. Type 304 Stainless Steel Tested at 1000 psi in Air at 1700°F. Discontinued after 523.5 hr of testing with 1.16% strain. Photograph taken of sample in as-polished condition. 500X.

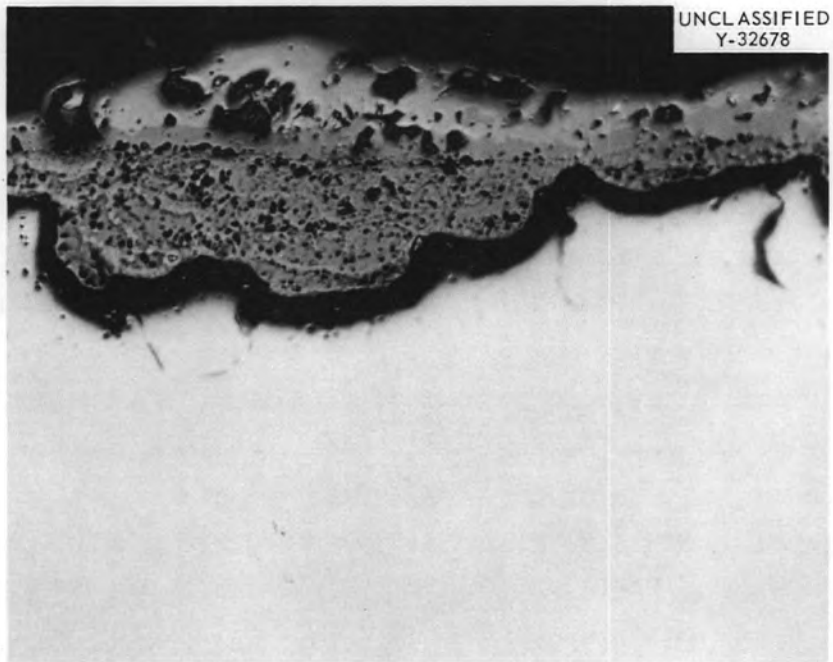

Fig. 12. Type 304 Stainless Steel Tested at 1200 psi in Air at 1700°F. Discontinued after 1004.8 hr of testing with 3.13% strain. Photograph taken of sample in as-polished condition. 500X.

Fig. 13. Type 304 Stainless Steel Tested at 1200 psi in Air at 1700°F. Failed after 1895.1 hr with 7.81% strain. Photograph taken of sample in as-polished condition. 200X.

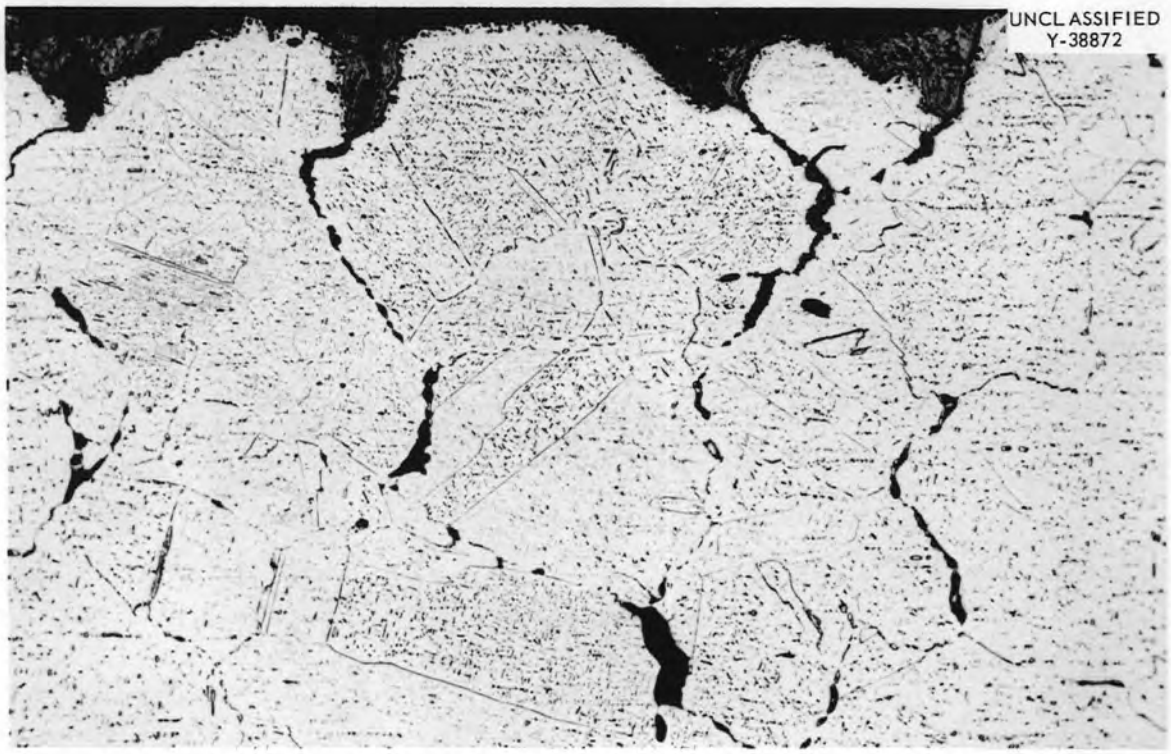

Fig. 14. Type 304 Stainless Steel Tested at 1500 psi in Air at 1700°F. Failed after 726 hr with 10.88% strain. Specimen etched lightly with aqua regia. 200X.

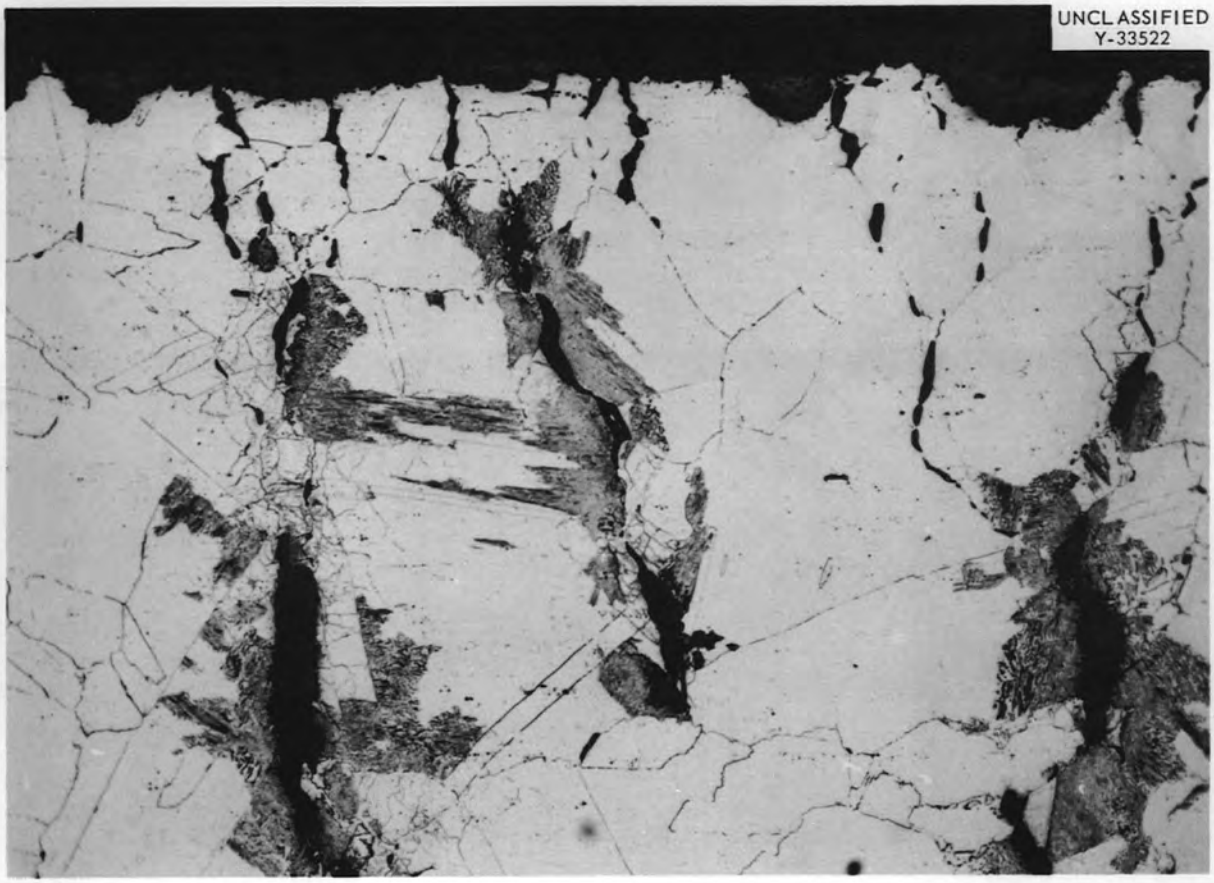

Fig. 15. Type 304 Stainless Steel Tested at 2500 psi in Air at 1700°F. Failed after 52.5 hr with 9.03% strain. Specimen etched lightly with aqua regia. 200X.

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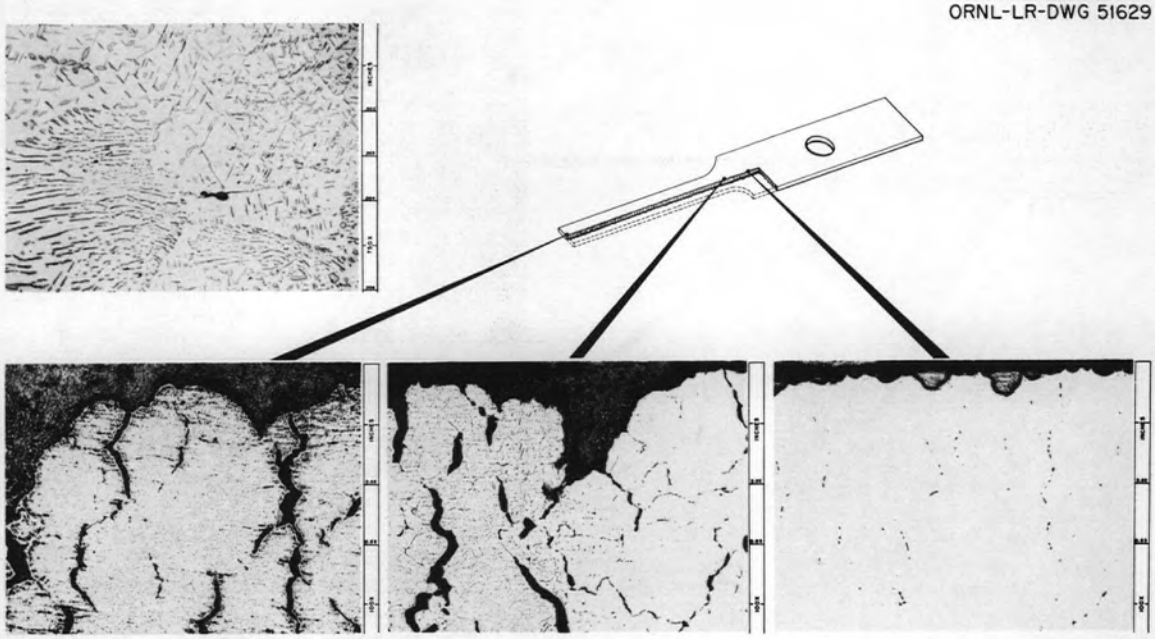


Fig. 16. Type 304 Stainless Steel Tested at 1500 psi in Air at 1700°F.

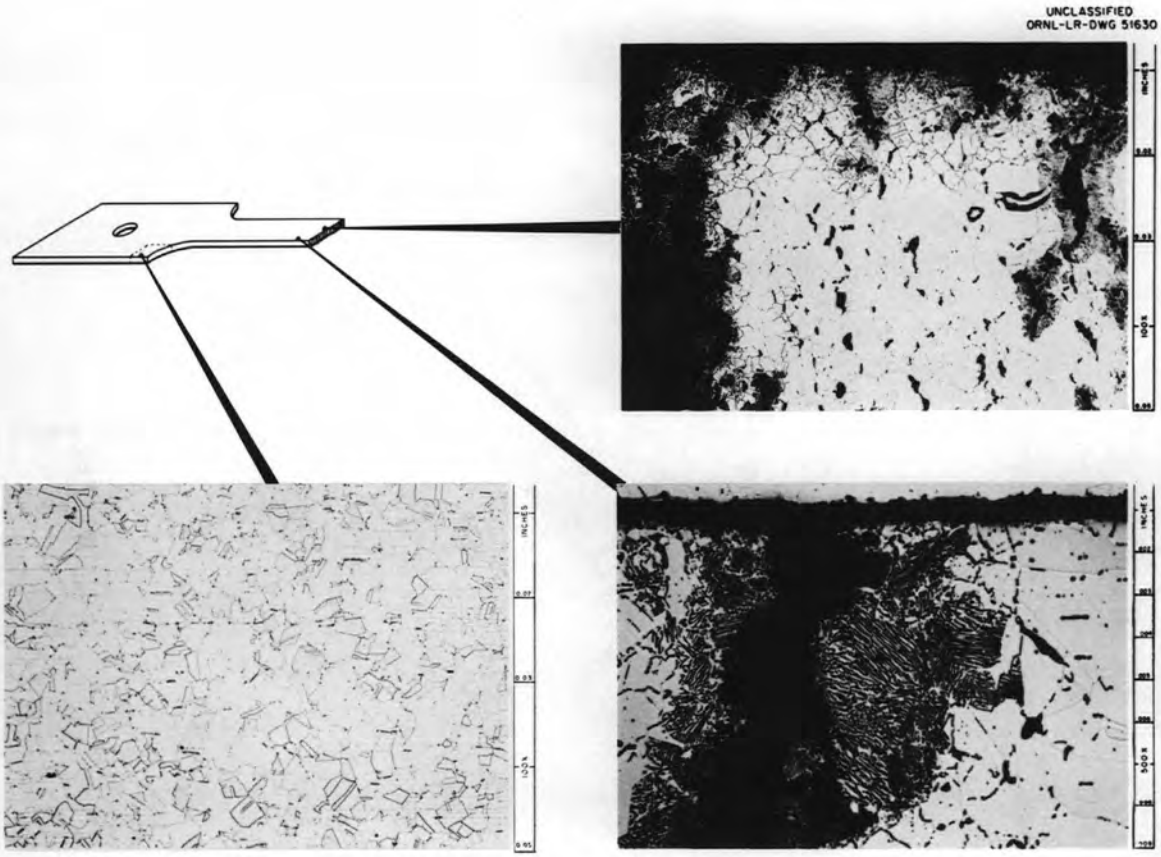


Fig. 17. Type 304 Stainless Steel Specimen Tested at 3400 psi in Nitrogen at 1500°F.

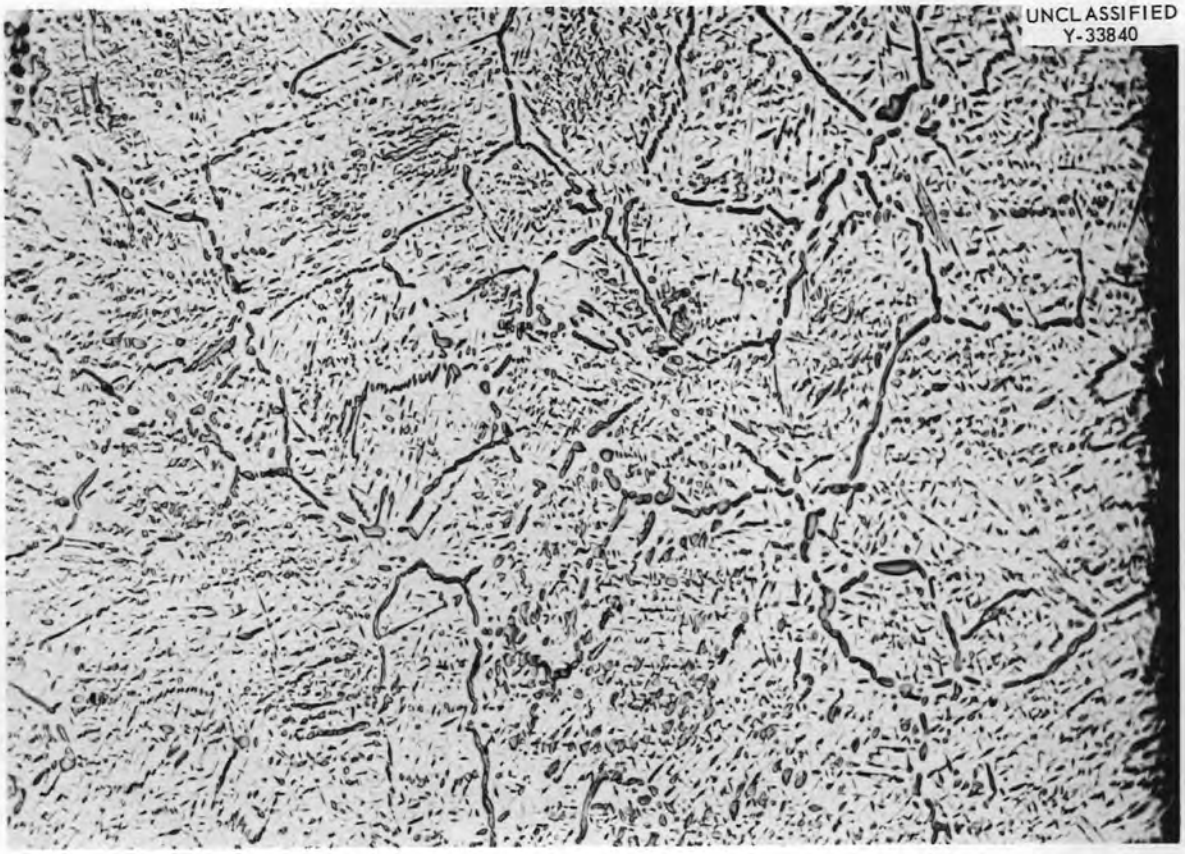


Fig. 18. Type 304 Stainless Steel Tested at 1200 psi in Nitrogen at 1700°F. Discontinued after 1554 hr of testing with 3.77% strain. Specimen etched with aqua regia. 200X.

Figure 19 is a photomicrograph of a specimen tested at 1500°F and 3000 psi in an oxygen environment. Note the presence of the second phase near the surface. This has been tentatively identified as ferrite by selective etching techniques.

Figure 20 is a photomicrograph of the edge of a specimen tested in CO at 1300°F. Three distinct layers are present. The first is an oxide layer formed at the gas-metal interface; the second is a layer composed of a lamellar product; and finally, there is a case of fine carbide particles which gradually diminish with distance into the matrix. The hardness is essentially constant across the specimen. On the basis of this observation, it seems probable that the lamellar layer is merely a different distribution of the carbide particles than that in the remainder of the case. It also indicates that the entire specimen is probably saturated with carbon so that the hardness is not appreciably changed by the presence of the relatively coarse carbide precipitate.

A microstructure characteristic of specimens tested in CO at 1500°F is shown in Fig. 21. This specimen was stressed at 3700 psi for 1731 hr. At this time the test was discontinued and the specimen was subjected to a standard tensile test at room temperature. Figure 21a shows the gage portion of the specimen and illustrates the case of fine carbide particles near the surface. Figure 21b is a photograph of the shoulder portion of the test specimen. Note the large concentration of voids near the surface. It is felt that these voids were originally filled by oxides which were lost during polishing. The loss of chromium near the surface to form surface oxides and carbides should result in an increase in the oxygen solubility. This would create an oxygen concentration gradient with the result that oxygen would diffuse inward.

At 1700°F the carbides become much coarser and the rate of carburization increases significantly. This is illustrated by Fig. 22 which is a photograph of the gage section of a specimen tested at 1200 psi in CO at 1700°F.

Specimens tested in CO_2 over the temperature range of 1300 to 1700°F were observed to be carburized. This is illustrated by Fig. 23 which is composed of photographs of a specimen tested at 3400 psi in CO_2 at 1500°F for 1727 hr. The test was discontinued and the specimen was subjected to

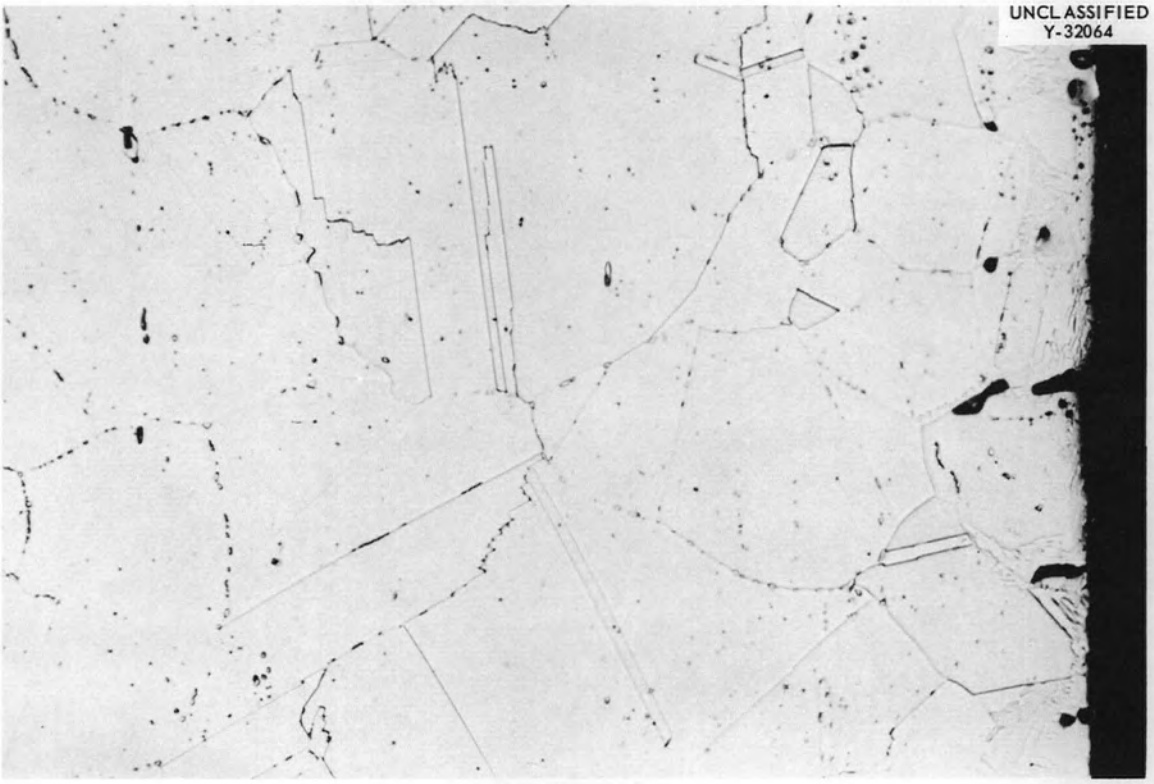


Fig. 19. Type 304 Stainless Steel Tested at 3000 psi in Oxygen at 1500°F. Test discontinued after 1247 hr with 4.55% strain. Specimen etched in glyceria regia. 500X. Reduced 8%.

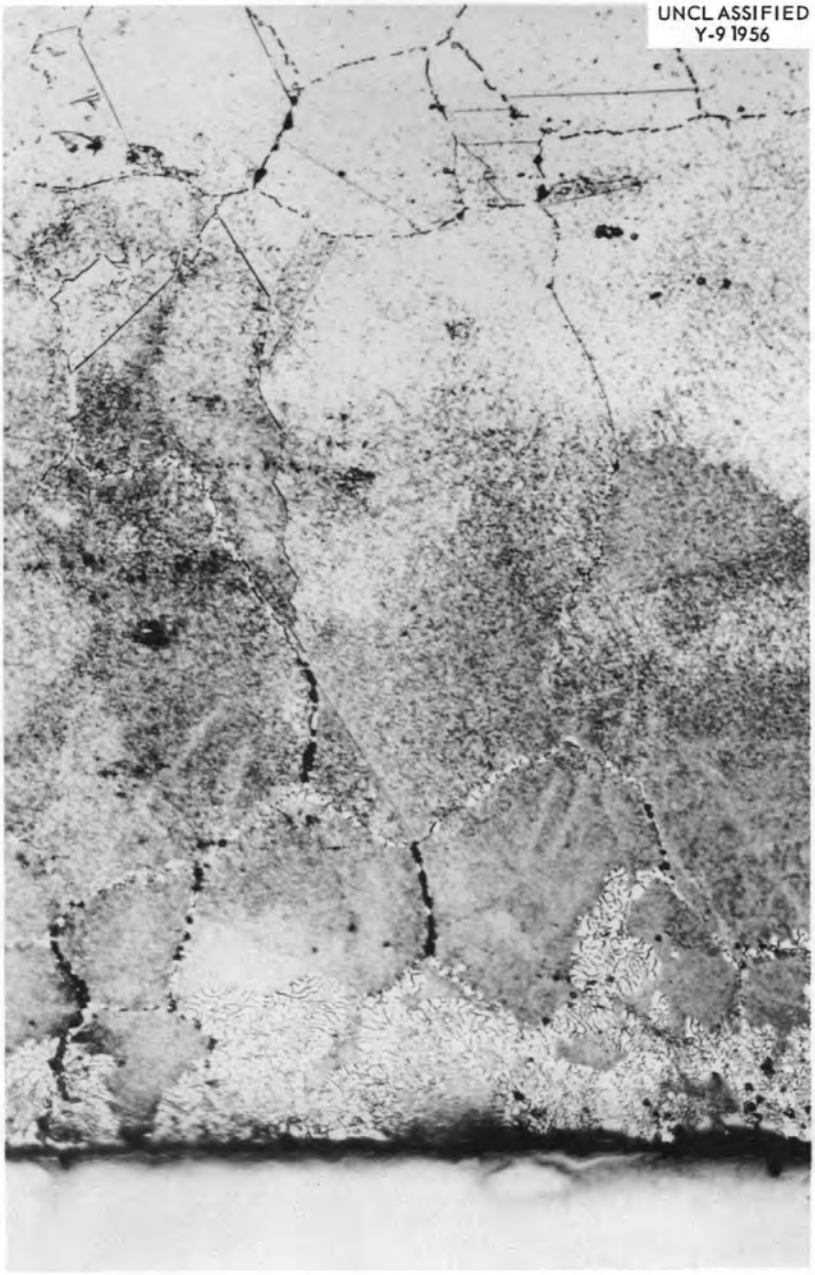
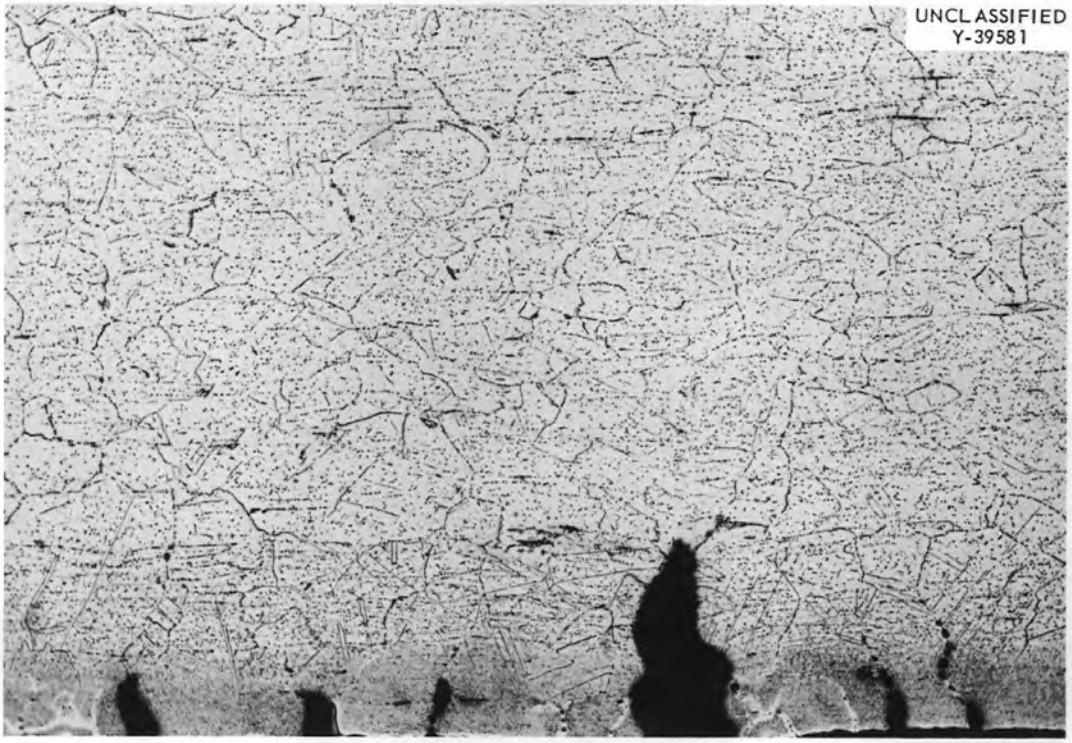
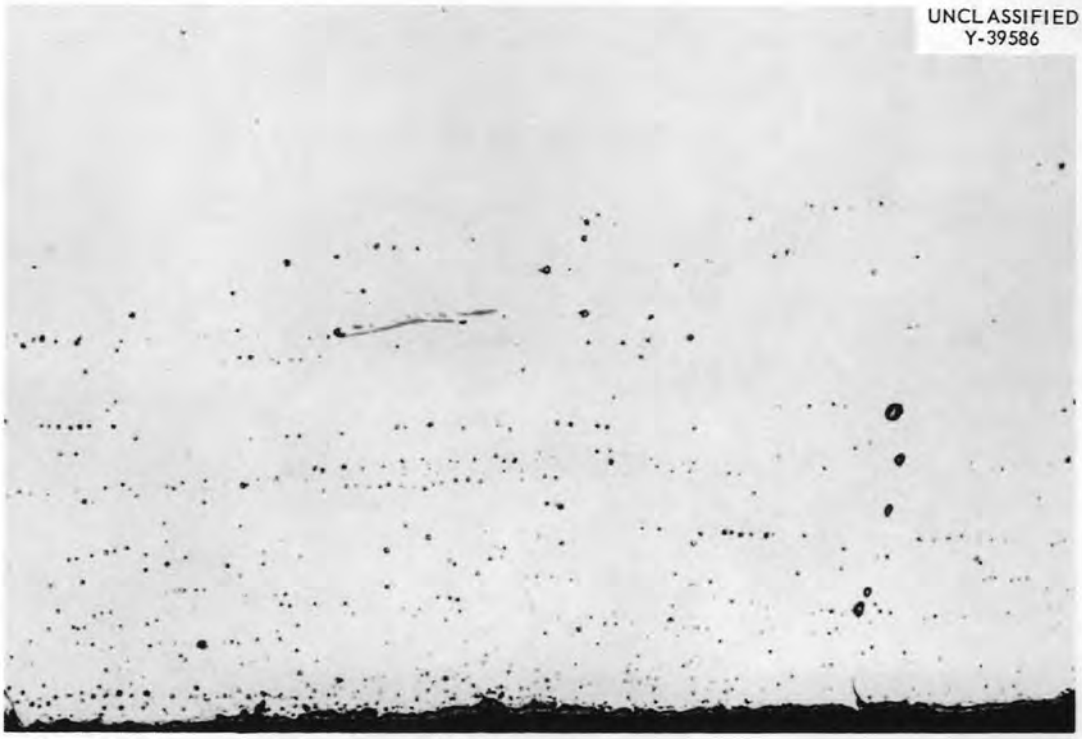


Fig. 20. Specimen Tested in Flowing CO at 1300°F and 9500 psi. Rupture Life: 672 hr. Etchant: glyceria regia. 500X.



(a) Gage Section



(b) Shoulder

Fig. 21. Photomicrographs of a Type 304 Stainless Steel Specimen Tested in Tension at Room Temperature. Strain rate was 0.0125 in./in./min. Prior to testing specimen was (1) annealed 1 hr at 1900°F in hydrogen and (2) loaded at 3700 psi in CO at 1500°F for 1731 hr. (a) 100X. (b) 500X.

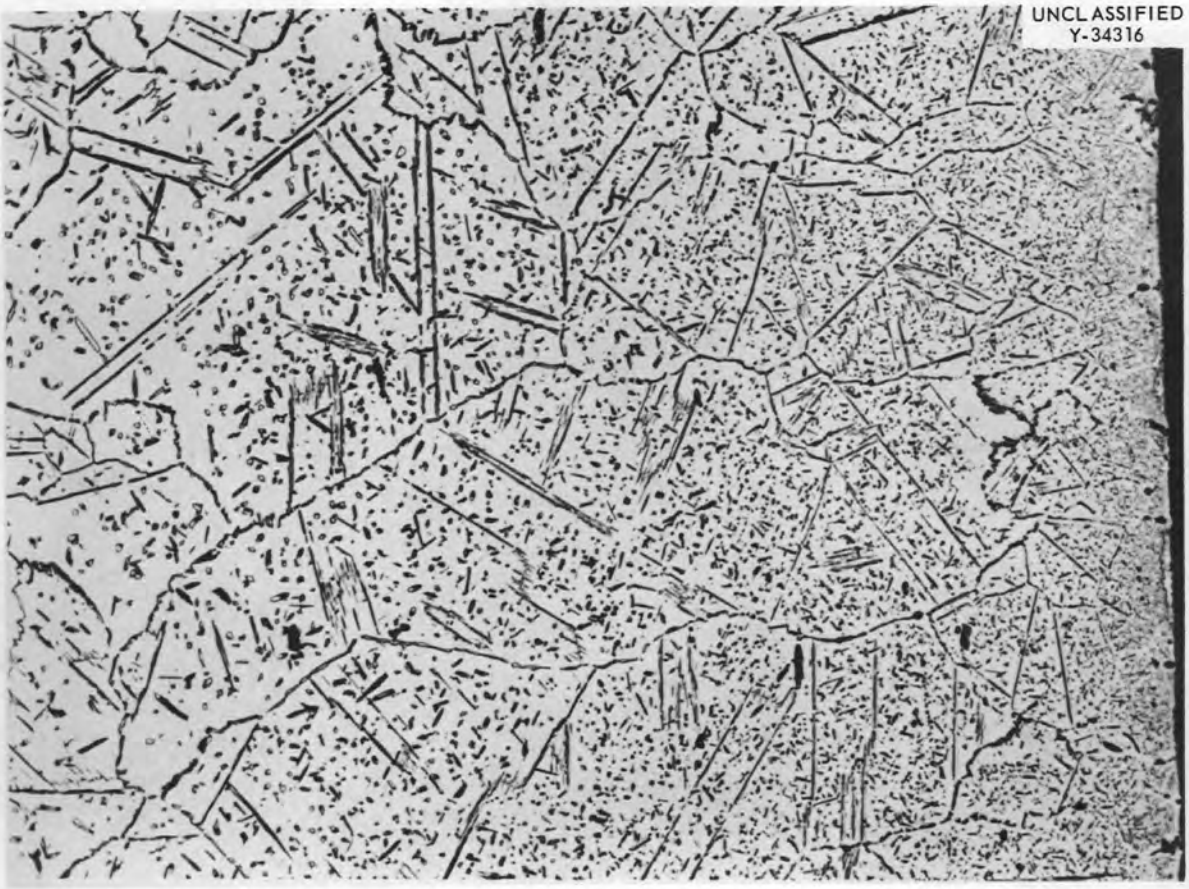
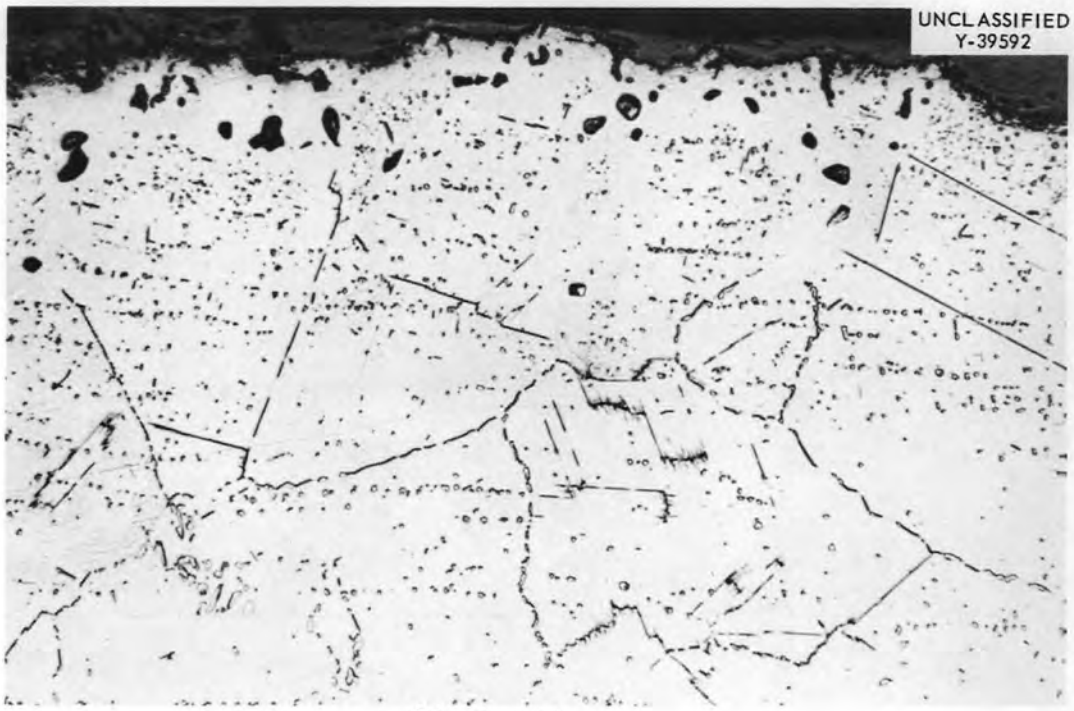


Fig. 22. Type 304 Stainless Steel Tested at 1200 psi in CO at 1700°F. Test discontinued after 335 hr with 1.57% strain. Etchant: 10% oxalic acid. 200X.

(a) Gage Section



(b) Shoulder

Fig. 23. Photomicrographs of a Type 304 Stainless Steel Specimen Tested in Tension at Room Temperature. Strain rate was 0.0125 in./in./min. Prior to testing specimen was (1) annealed 1 hr at 1900°F in hydrogen and (2) loaded at 3400 psi in CO_2 at 1500°F for 1727 hr. Etchant: aqua regia. (a) 100X. (b) 500X.

a standard room-temperature tensile test. Figure 23a shows the gage section of this specimen. There is evidence of considerable carburization although no case is visible. Figure 23b shows an edge of the shoulder portion of the specimen and illustrates the large subsurface voids which were formed. It is presently felt that the explanation presented for the appearance of Fig. 21b is applicable in this case, also.

Chemical and Hardness Data

Chemical composition and hardness data obtained from the test specimens are supplementary information which is useful in rationalizing the observed creep behavior. Vacuum fusion analyses of several of the test specimens are given in Table 4. Analytical samples were cut from the gage length of the specimen and were analyzed both with and without surface cleaning.

Table 4. Vacuum Fusion Analyses of Type 304 Stainless Steel Specimens After Test

Test Conditions					Analysis After Test		Analysis After Test[a]	
Test No.	Stress (psi)	Temperature (°F)	Environment	Duration of test (hr)	O_2 (wt %)	N_2 (wt %)	O_2 (wt %)	N_2 (wt %)
327	3400	1500	Ar	1000.7	0.016	0.036	0.016	0.036
					0.021	0.032	0.011	0.031
260	3000	1500	Air	1436.8	0.33	0.039	0.018	0.036
315	3400	1500	Air	3024.6	0.37	0.031	0.035	0.040
330	3400	1500	Air	1005.2	0.22	0.048	0.015	0.045
266	3000	1500	O_2	1247.2	0.089	0.031	0.013	0.031
316	3400	1500	O_2	989.7	0.13	0.040	0.079	0.035
					0.30	0.032	0.037	0.035
318	1200	1700	Air	1895.1	0.64	0.18	0.35	0.18
10	1200	1700	N_2	1554.0	0.031	1.30	0.028	1.20

[a]Surface film removed.

Several specimens, particularly those run in carburizing atmospheres, were analyzed for carbon after testing. These results are given in Table 5. Analytical specimens were cut both from the shoulder and gage sections of the specimens.

Table 5. Carbon Analyses of Specimens After Testing

Material: Heat C

Temperature (°F)	Stress (psi)	Environment	Rupture Life (hr)	Strain (%)	Copper Plated	Carbon Content (wt %) Shoulder	Carbon Content (wt %) Gage
1300	9500	CO	1025	17.96	Yes	0.047	0.065
1300	9500	CO	672	12.50	No	0.122	0.130
1500	3400	a	992	13.00	Yes	0.048	0.071
1500	3400	CO	1939[b]	8.98	Yes	2.43	3.15
1700	1200	CO	335[b]	1.57	No	1.01	1.31
1700	1200	CO	1964[b]	9.54	Yes	3.84	6.06
1500	3400	CO_2	1005[b]	1.56	No	0.17	0.18
1500	3000	CO_2	1266[b]	2.31	No	0.16	0.18

[a] 1 CO–1 CO_2–Ar (vol %).

[b] Test discontinued prior to failure.

Table 6 summarizes the hardness data obtained from metallographic specimens. The values given are the ranges and averages of from 6 to 10 impressions. Where the range was due to the presence of a carbide or nitride case, the values were not averaged. The specimen location refers to the position of the test specimen from which the sample was cut. Location No. 1 is the fracture and about $\frac{1}{2}$ in. of the gage section. Location No. 2 is the next 1 in. of material adjacent to No. 1. Location No. 3 is the corner of the specimen shoulder nearest the gage section.

Effect of Carbon on the Ductility of Type 304 Stainless Steel

A limited number of tensile tests have been run to evaluate the influence of carburization on the ductility of type 304 stainless steel. The results of one series of tests on 0.060-in.-thick specimens are given in Table 7. Carbon additions of up to 0.28 wt % reduced the room-temperature rupture ductility from 83 to 11%. Similar additions reduced the rupture ductility at 1500°F from 35 to 19%. Figure 24 is a photomicrograph of the gage section of specimen No. 1. Specimen Nos. 2 and 3 are illustrated in Figs. 23 and 21, respectively. Note that the deformation in specimen No. 1 occurred fairly uniformly along the gage section by

Table 6. Hardness Measurements on Test Specimens

Temperature (°F)	Environment	Exposure Time (hr)	Specimen Location	Hardness, DPH Range	Hardness, DPH Average
1300	CO_2	672	No. 1	143–420	--
1500	Ar	224	No. 2	122–141	130
1500	Air	1437	No. 1	125–135	130
1500	Air	3025	No. 2	143–161	150
			No. 3	121–145	130
1500	O_2	1247	No. 1	128–145	132
1500	CO	1731	No. 3	143–187	--
1500	CO	929	No. 1	161–189	--
1500	CO_2	1727	No. 3	144–171	--
1500	CO_2	1005	No. 1	156–169	--
1500	a	992.4	No. 1	148–182	--
			No. 3	125–143	130
1700	Ar	379	No. 1	120–125	122
1700	H_2	165	No. 1	120–141	130
1700	Air	1005	No. 1	125–131	128
1700	Air	739	No. 2	149–266	--

[a]1 CO–1 CO_2–Ar (vol %).

Table 7. Tensile Data Showing the Effects of Carbon on the Tensile Properties of Type 304 Stainless Steel Sheet Specimens

Specimen No.	Specimen History[a]	Test Temperature (°F)	Yield Strength (psi)	Tensile Strength (psi)	Elongation % in 2 in.	Average Carbon Content (wt %)
1	As annealed	75	26,500	87,100	83	0.033
2	Tested at 3400 psi and 1500°F in CO_2 for 1727 hr	75	25,000	79,900	60	0.093
3	Tested at 3700 psi and 1500°F in CO for 1731 hr	75	30,200	81,000	23	0.21
4	Carburized 233 hr at 1500°F in CO	75	32,600	76,300	11	0.23
5	Carburized 500 hr at 1500°F in CO	75	34,300	83,900	11	0.28
6	As annealed	1500	10,500	19,500	35	0.033
7	Carburized 233 hr at 1500°F in CO	1500	16,800	25,600	37	0.23
8	Carburized 500 hr at 1500°F in CO	1500	18,400	25,800	25	0.28
9	Carburized 500 hr at 1500°F in CO, homogenized 1 hr at 1900°F in argon	1500	17,600	25,100	19	0.28

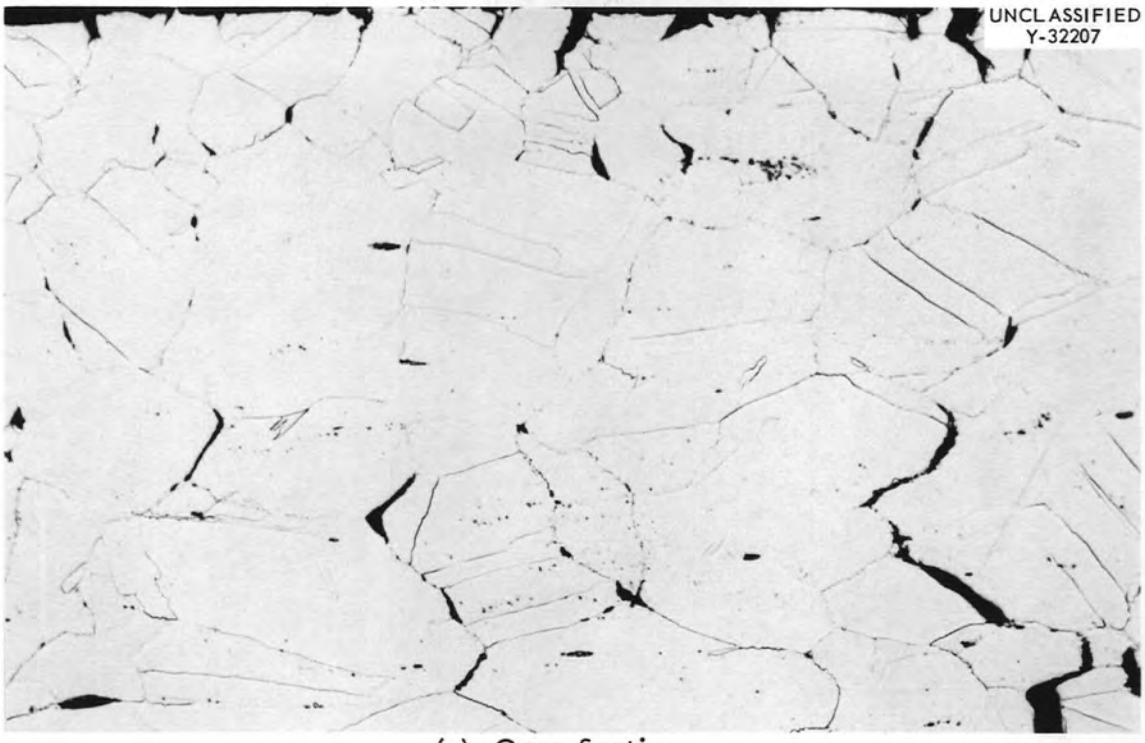
[a]All specimens given a 1-hr anneal at 1900°F in hydrogen prior to the indicated treatment.

Fig. 24. Photomicrograph of the Gage Section of a Type 304 Stainless Steel Specimen Tested in Tension at Room Temperature. Strain rate was 0.0125 in./in./min. Annealed 1 hr at 1900°F in hydrogen prior to test. Etchant: aqua regia. 100X.

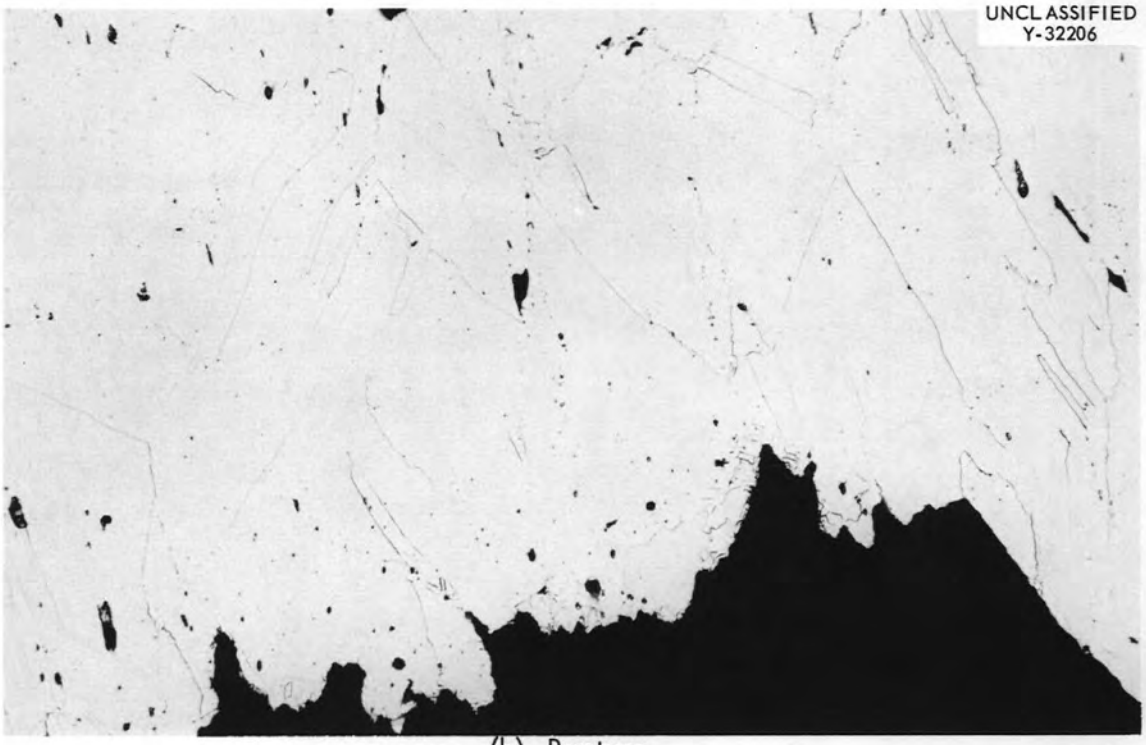
slip. In specimen Nos. 2 and 3 deformation occurred largely by intergranular cracking and plastic deformation was mostly confined to a relatively small area near the fracture. Much of the intergranular cracking was probably nucleated during the 1700-hr creep test at 1500°F to which specimen Nos. 2 and 3 were subjected prior to the room-temperature tensile test.

Figures 25, 26, and 27 are photomicrographs representative of specimen Nos. 6, 7, and 8 (see Table 7). Again the differences in deformation modes as brought about by increasing the carbon content are obvious. The specimen which contained 0.033 wt % C shows evidence of deformation by grain-boundary shear movements and by slip. This is illustrated in Fig. 25. Note the distorted grain boundaries, the mottled appearance of some areas as a result of nonuniform etching characteristics, and the recrystallization which occurred along the grain boundaries, particularly near the rupture. The specimens containing larger amounts of carbon, Nos. 7 and 8, did not exhibit the same characteristics. There is no evidence of the grain-boundary shear movements as observed in specimen No. 6. Note in Figs. 26 and 27 that no recrystallization occurred near the grain boundaries nor is there the mottled appearance of some areas which indicate large amounts of cold working. However, the carbides present decorate the slip lines and show that this mechanism was operative during deformation. The extensive quantities of carbides present are probably responsible for limiting the extent of grain-boundary movements in the samples containing 0.2 to 0.3 wt % C.

The results of a similar series of tests using 0.020-in.-thick sheet specimens are shown in Fig. 28. These specimens were carburized in CO at 1500 and 1900°F and were tested in tension at room temperature. The carbon content plotted on the ordinate is the average carbon concentration of a cross section of the material. Specimens carburized at 1900°F were reasonably homogeneous, whereas the major portion of the carbon present in those specimens carburized at 1500°F was concentrated near the surface. The latter type of carbon distribution results in a greater reduction in the ductility than an equivalent amount of carbon distributed more evenly.

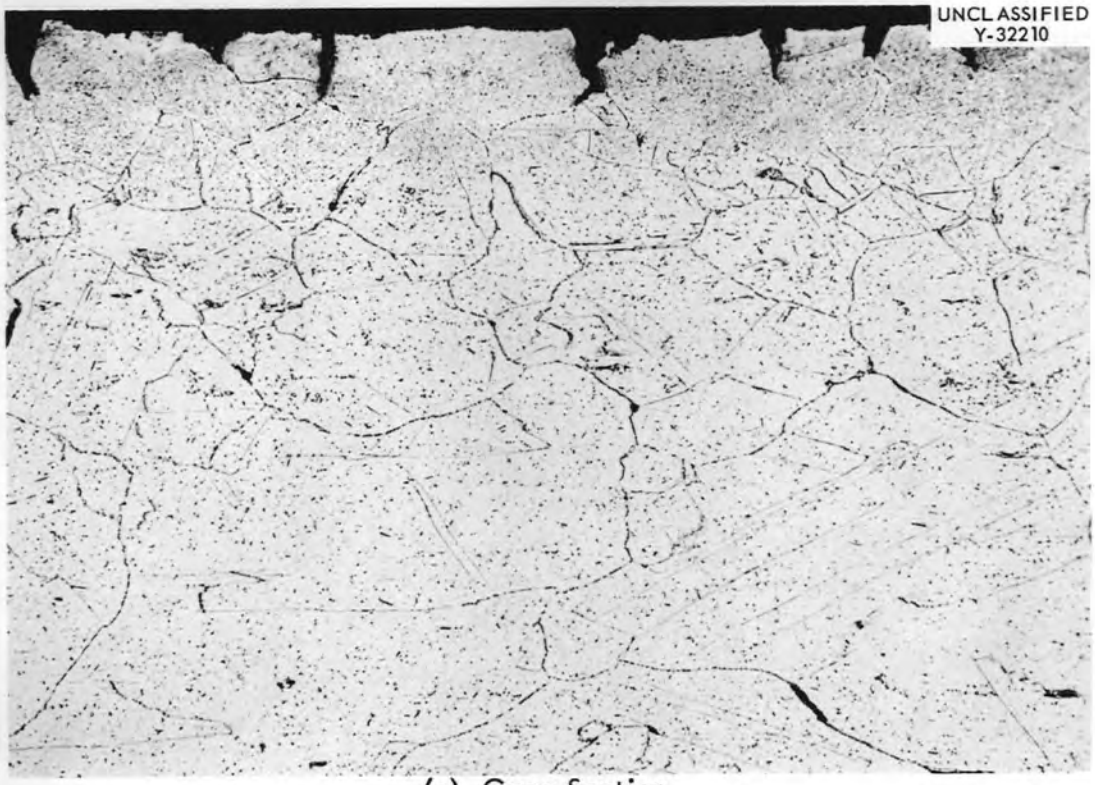


(a) Gage Section

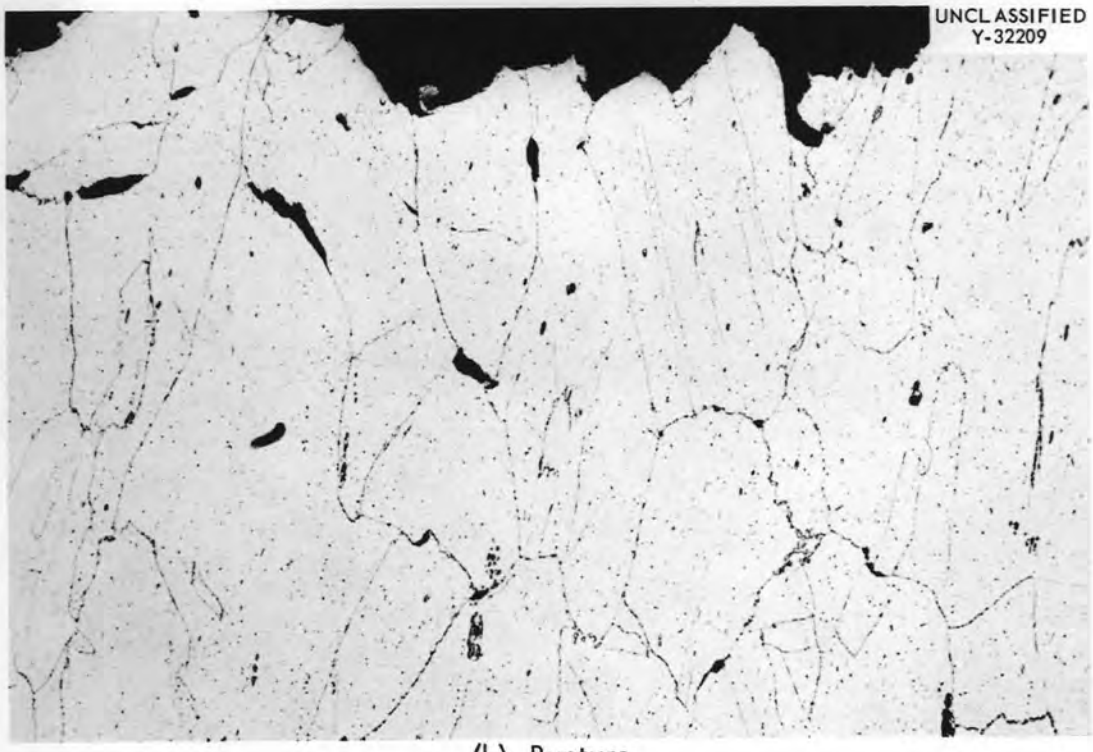


(b) Rupture

Fig. 25. Photomicrographs of a Type 304 Stainless Steel Specimen Tested in Tension at 1500°F in Air. Strain rate was 0.0125 in./in./min. Prior to test, specimen was annealed 1 hr at 1900°F in hydrogen. Etchant: glyceria regia. 200X.

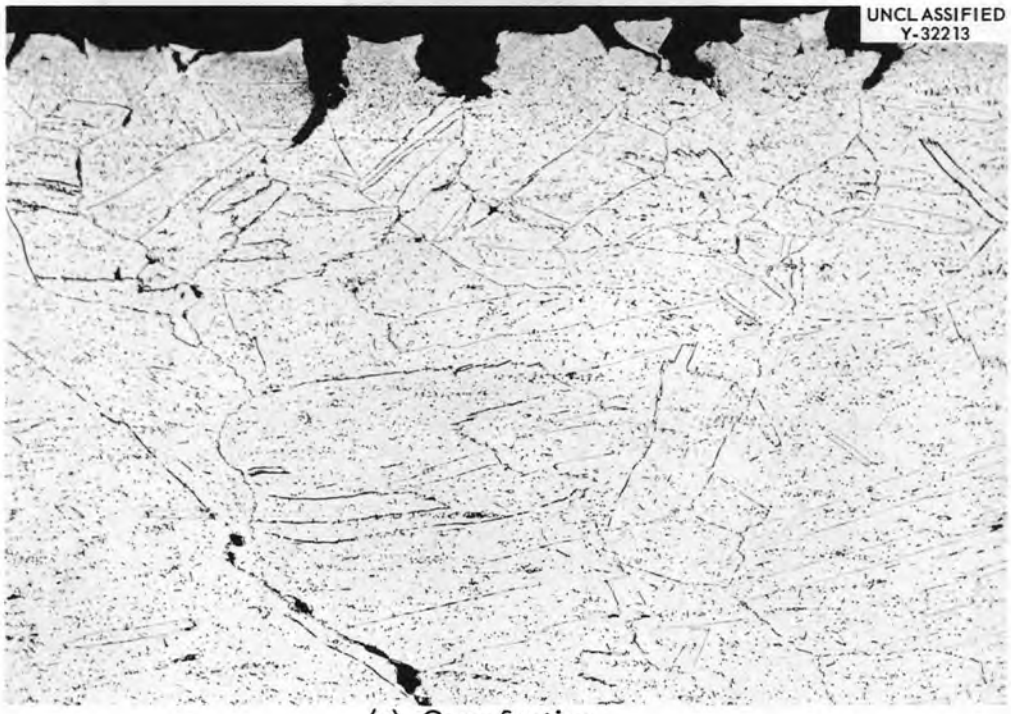


(a) Gage Section

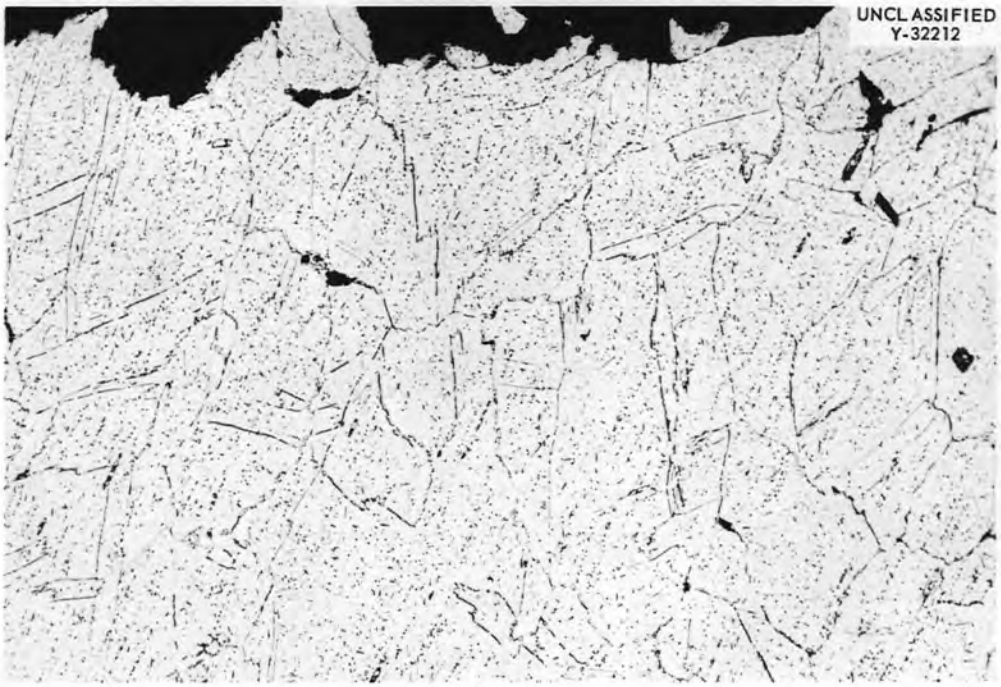


(b) Rupture

Fig. 26. Photomicrographs of a Type 304 Stainless Steel Specimen Tested in Tension at 1500°F in Air. Strain rate was 0.0125 in./in./min. Prior to test, specimen was (1) annealed 1 hr at 1900°F in hydrogen and (2) annealed 233 hr in CO at 1500°F. Etchant: glyceria regia. 200X.



(a) Gage Section



(b) Rupture

Fig. 27. Photomicrographs of a Type 304 Stainless Steel Specimen Tested in Tension at 1500°F in Air. Strain rate was 0.0125 in./in./min. Prior to test, specimen was (1) annealed 1 hr at 1900°F in hydrogen and (2) annealed 500 hr in CO at 1500°F. Etchant: glyceria regia. 200X Reduced 8%.

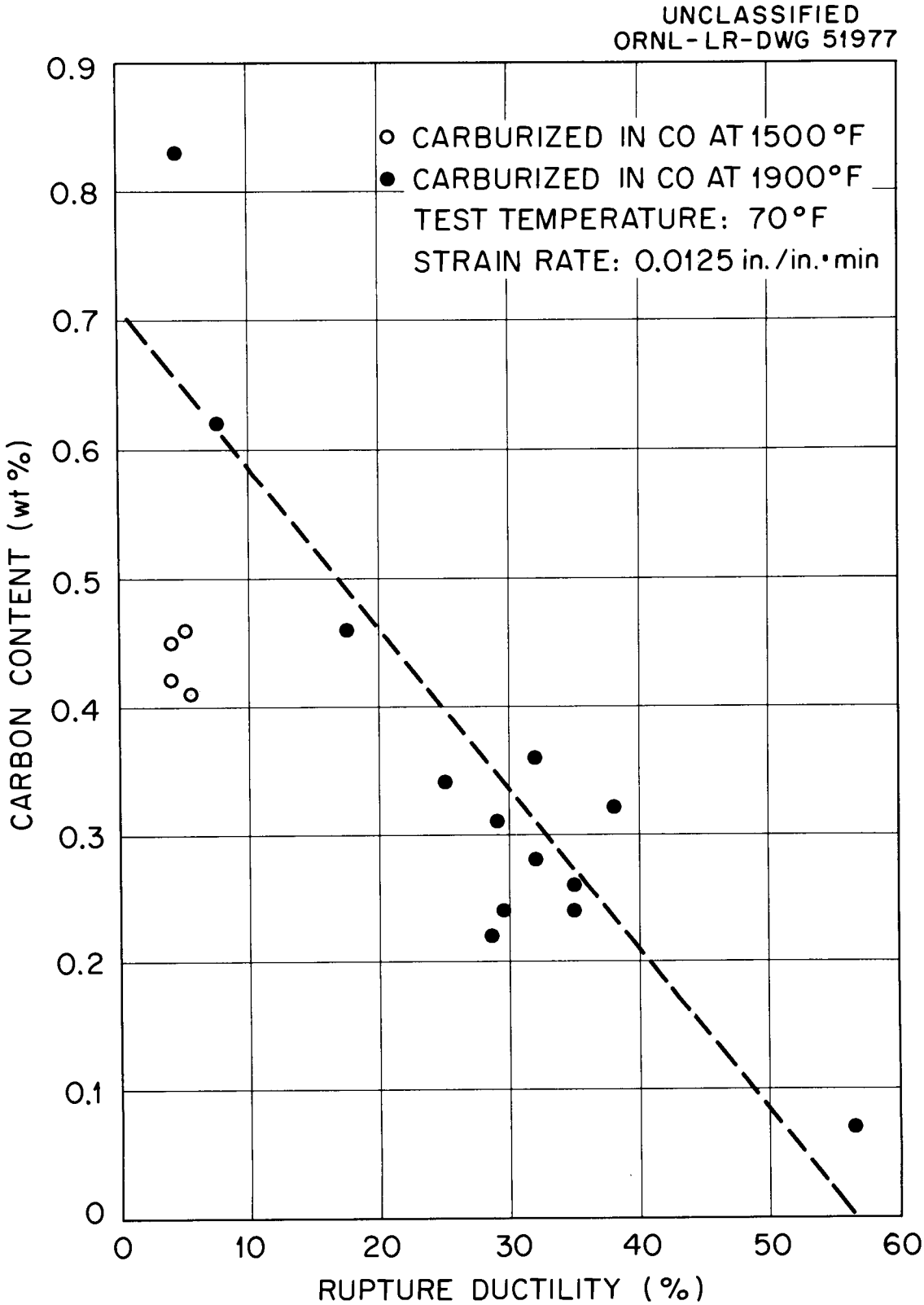


Fig. 28. Effect of Carbon on the Rupture Ductility of Type 304 Stainless Steel.

Use of Copper Films to Inhibit Carburization

It may be desired that the carburization of certain critical parts be completely eliminated. The extremely low solubility of carbon in copper (reported by Bever and Floe[3] to be about 0.0001 wt % at 1100°C) and the ease with which parts can be coated with copper electrolytically were responsible for the investigation of the effectiveness of copper for inhibiting carburization in CO and CO_2. Tests on several unstressed tabs of type 304 stainless steel which had been coated with 0.001 in. of copper were encouraging. A series of specimens run in CO_2 at 1500°F is shown in Fig. 29. Note that some deterioration of the film occurred probably as a result of the oxidizing potential of CO_2. However, no carburization occurred as evidenced by metallographic and chemical analyses. Similar tabs tested in CO did not show evidence of oxidation but were carburized. For example, the carbon content of an 0.020-in.-thick specimen tested in CO for 215 hr at 1500°F increased from 0.047 to 0.083 wt %.

Creep specimens were also plated for evaluating the integrity of the coating during deformation. The results of these tests at 1300, 1500, and 1700°F are evidenced by the after-test analytical data in Table 5 and by Figs. 30–36. A series of photomicrographs of a specimen tested at 9500 psi in CO is shown in Fig. 30. The specimen was in test for 1025 hr and underwent 17.96% strain. The coating seems to have completely eliminated carburization of the shoulder of the specimen where essentially no strain occurred. However, several breaks occurred in the coating on the gage section of the specimen and small amounts of localized carburization resulted. Nevertheless, the creep curves in Fig. 31 indicate that the resulting carburization did not significantly alter the creep properties of the material. Hence, the breaks in the film and the initiation of carburization probably occurred during the last few hours of the test.

At 1500°F the copper coating was quite effective in reducing carburization in an environment of 1 CO–1 CO_2–Ar (vol %). Photomicrographs of the shoulder and gage sections of this specimen are shown in Fig. 32. However, the degree of protection obtained at 1500°F in an environment

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[3]M. B. Bever and C. F. Floe, Trans. Met. Soc. AIME 166, 128–41 (1946).

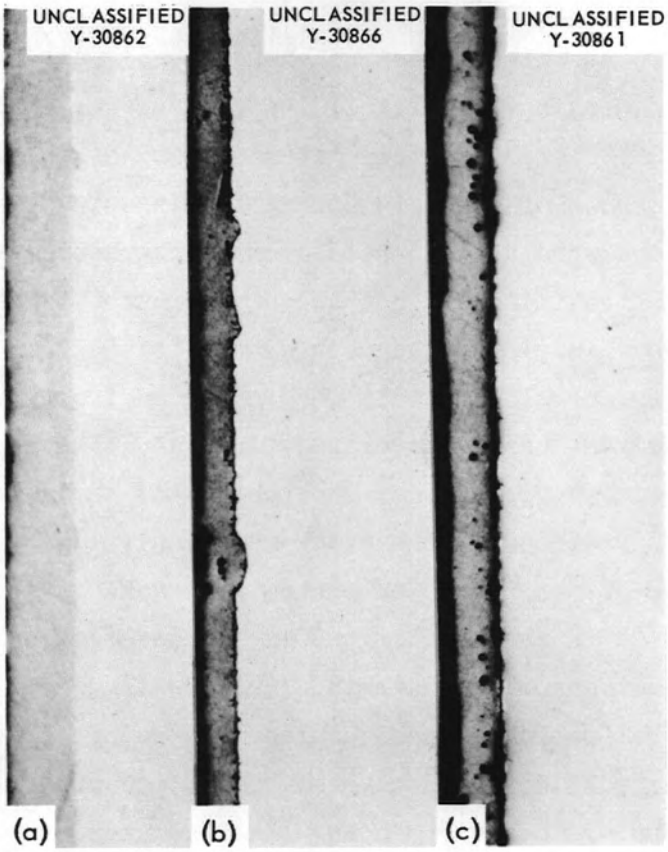


Fig. 29. Compatibility of Copper-Plated Type 304 Stainless Steel with CO_2 at 1500°F. Test conditions as follows: (a) as plated, (b) 24 hr in CO_2 at 1500°F, (c) 193 hr in CO_2 at 1500°F. 200X.

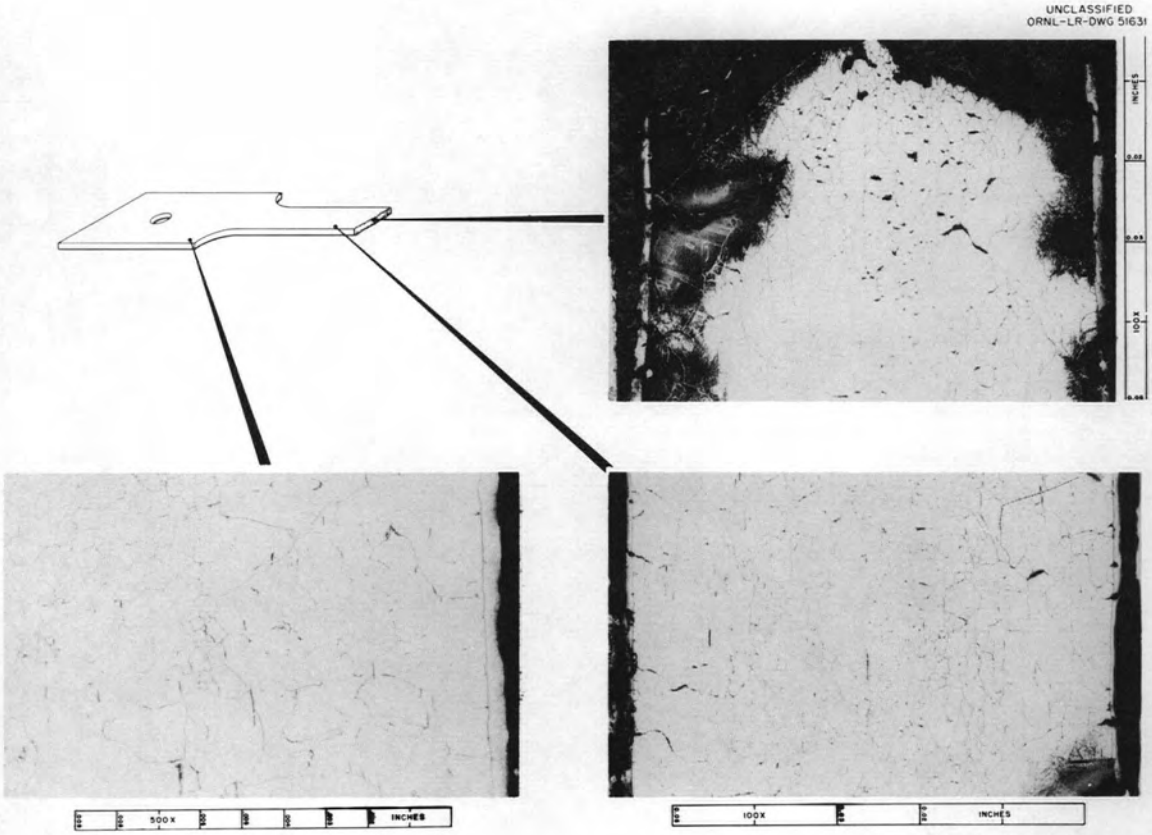


Fig. 30. Type 304 Stainless Steel Specimen Copper Plated and Tested at 9500 psi in CO at 1300°F.

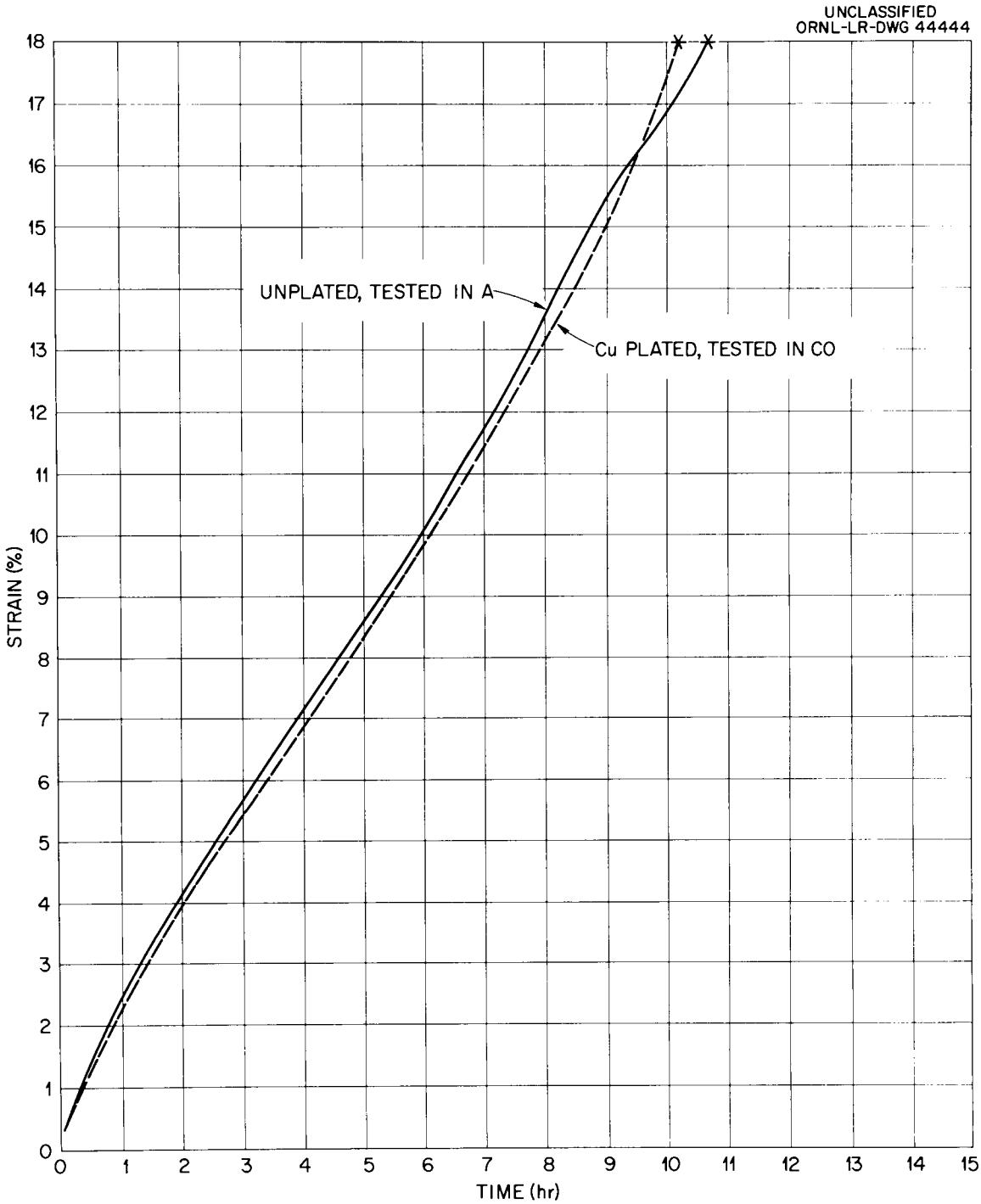
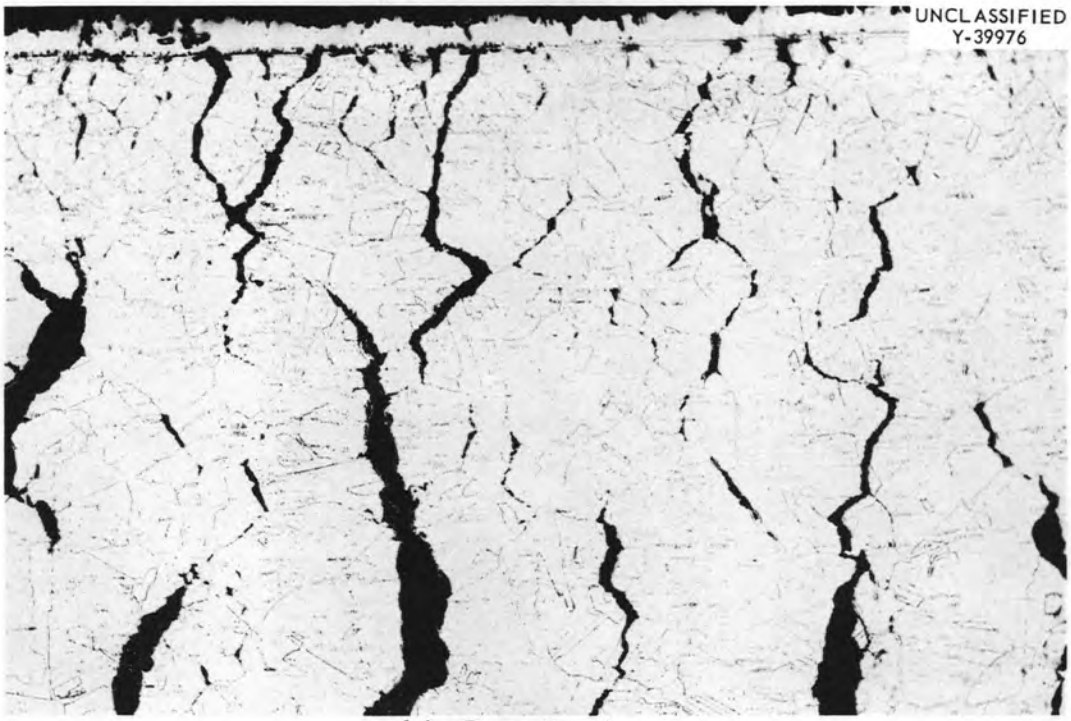


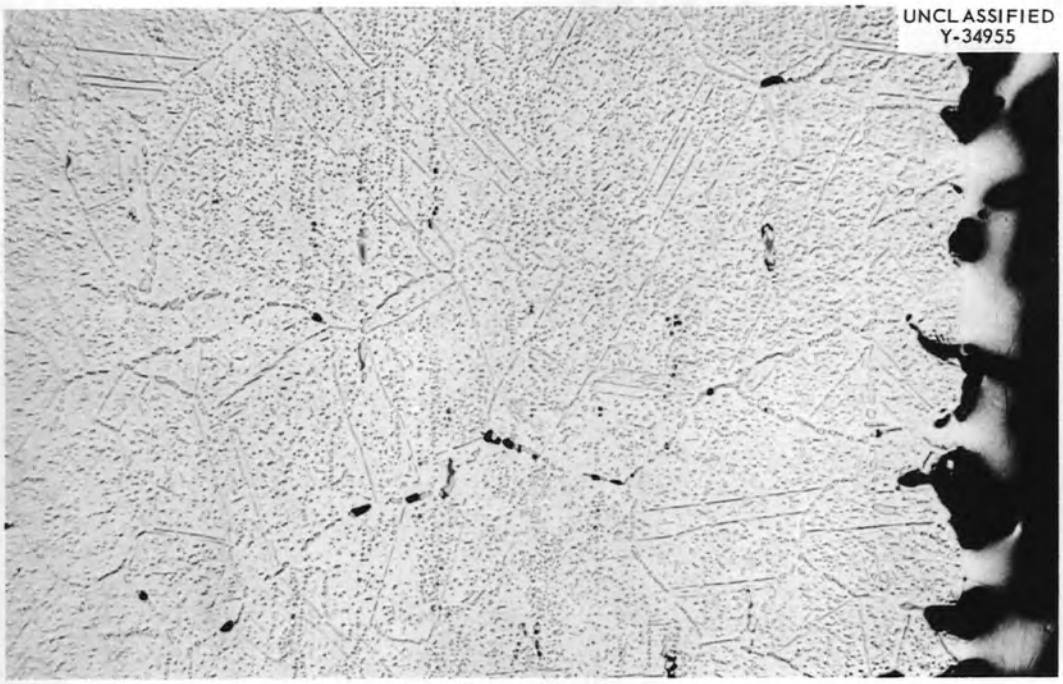
Fig. 31. Effect of Copper Plating on the Creep Properties of Type 304 Stainless Steel in CO at 1300°F and 9500 psi.



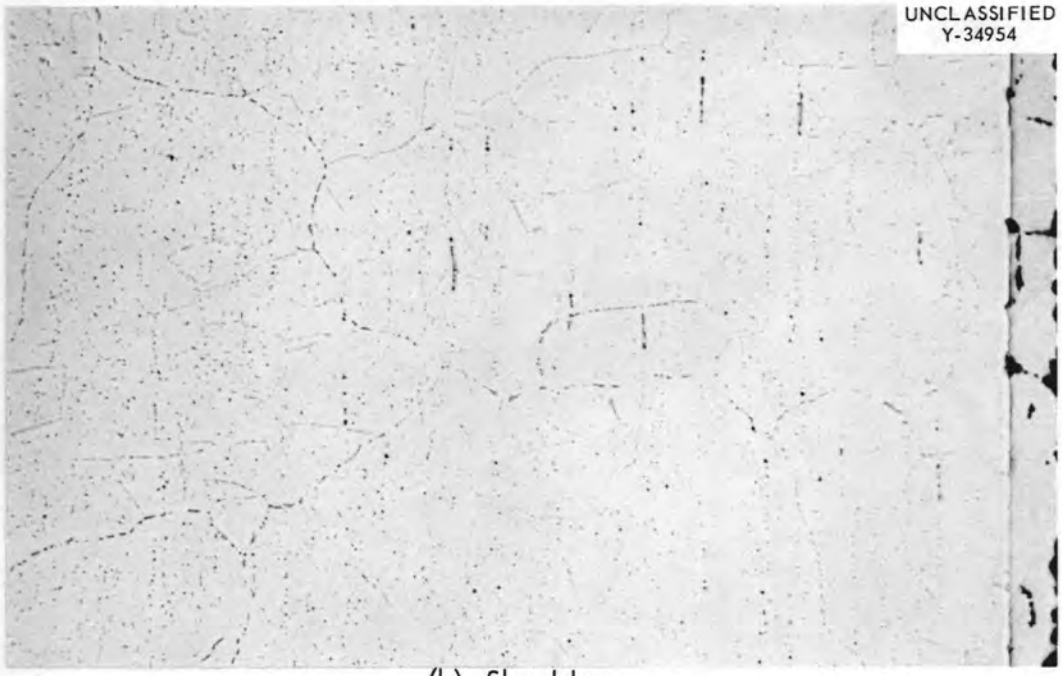
(a) Gage Section

(b) Shoulder

Fig. 32. Type 304 Stainless Steel Tested at 3400 psi and 1500°F in an Atmosphere of 1 CO–1 CO_2–98 Ar (vol %). Specimen plated with approximate 0.001 in. of copper before test. Failure occurred after 992 hr and 13.0% strain. Etchant: aqua regia. 100X.



(a) Gage Section



(b) Shoulder

Fig. 33. Type 304 Stainless Steel Tested at 3400 psi in CO at 1500°F. Specimen plated with approximately 0.001-in. copper before testing. Test discontinued after 1939 hr and 9.0% strain. Etchant: aqua regia. 200X

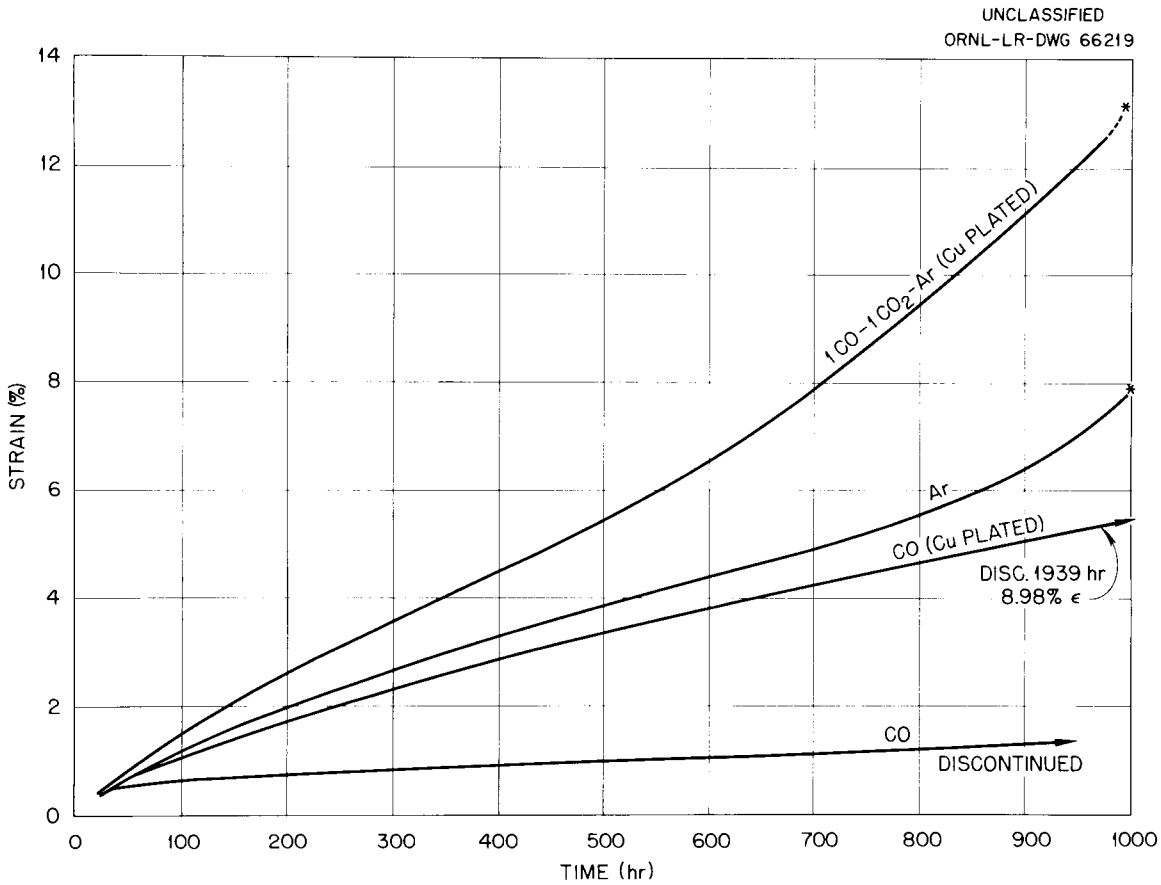
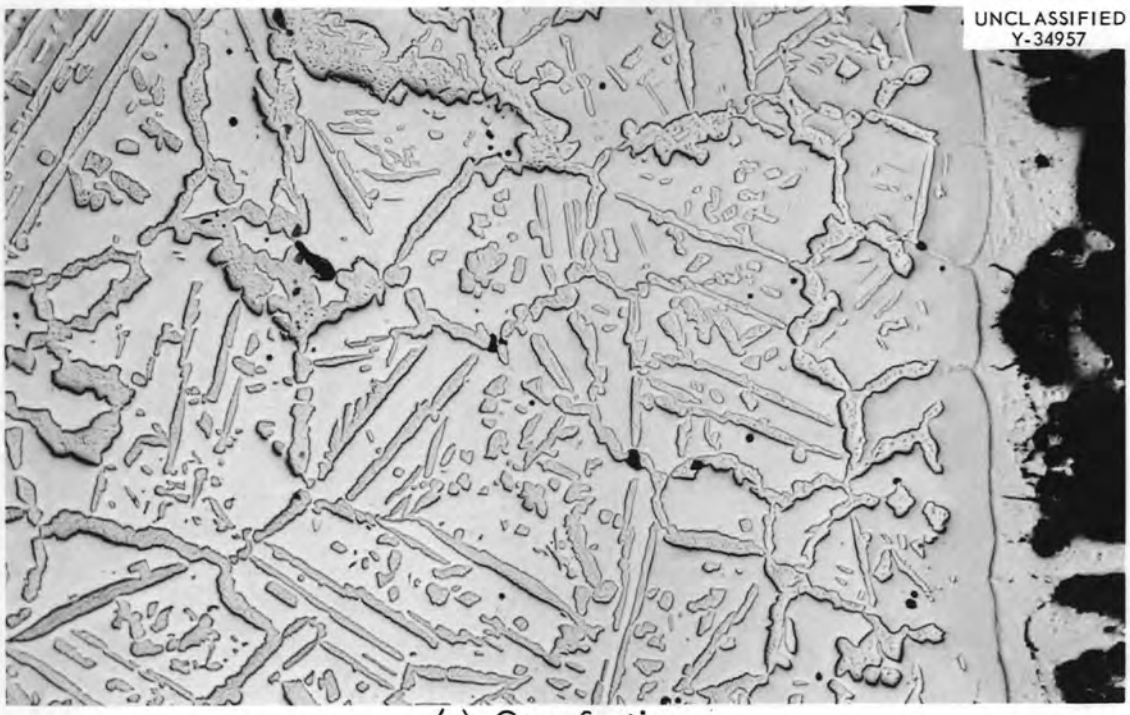
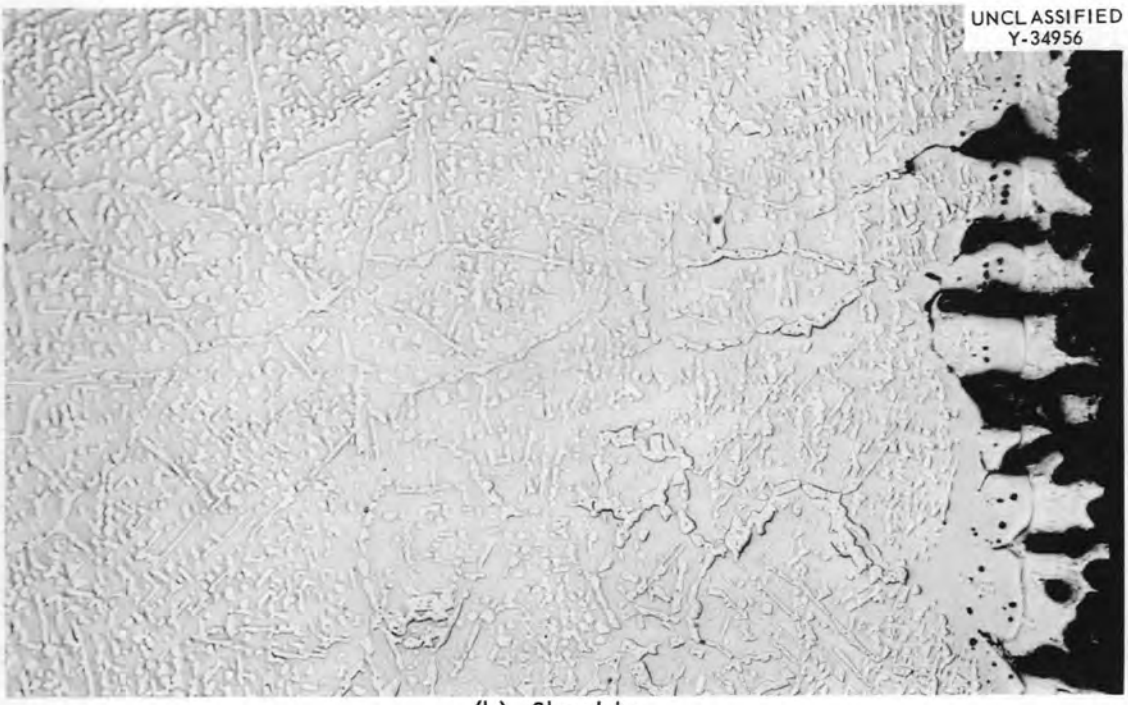


Fig. 34. Effect of Copper Plating on the Creep Properties of Type 304 Stainless Steel in CO at 1500°F and 3400 psi.



(a) Gage Section



(b) Shoulder

Fig. 35. Photomicrographs of a Type 304 Stainless Steel Specimen Tested at 1200 psi in CO at 1700°F. Specimen was coated with approximately 0.001 in. of copper before testing. Test was discontinued after 1964 hr with 9.54% strain. Photographs made of sample in as-polished condition. 200X.

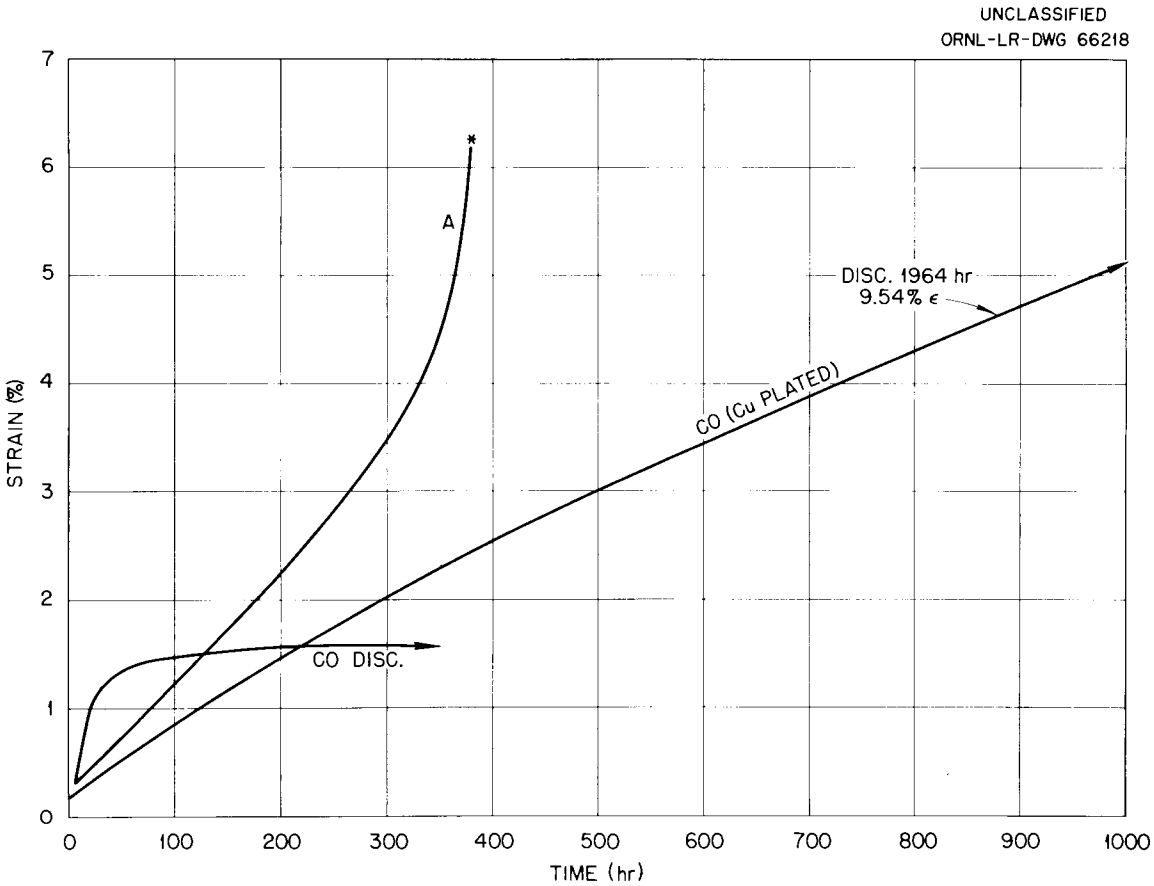


Fig. 36. Effect of Copper Plating on the Creep Properties of Type 304 Stainless Steel in CO at 1700°F and 1200 psi.

of CO at 1 atm pressure is limited. Figure 33 illustrates this point. Note that even the coating on the shoulder portion of the sample shows some deterioration with resulting carburization. Figure 34 shows a comparison of the creep behavior of several specimens in carburizing environments at 1500°F. These curves again demonstrate the inability of copper coatings to completely prevent carburization at 1500°F, but at the same time illustrate the decrease in carburization rate brought about by copper.

The effectiveness of copper films at 1700°F is quite analogous with that observed at 1500°F. A reduction in carburization rate is observed, but carburization is not entirely prevented. This is illustrated by the photographs in Fig. 35 and the creep curves shown in Fig. 36.

DISCUSSION OF RESULTS

The magnitude of the effects noted in this investigation stimulates a desire to understand the mechanisms which alter the behavior of the metal. Most of the changes in properties which occur as a result of nitriding or carburizing seem to be explained by the theories of dispersion hardening in relation to creep. The enhancement of creep properties which can be obtained through carburization and nitriding has been demonstrated by Swindeman and Douglas.[4]

The current results show that the magnitude of the enhancement of creep properties in a carburizing environment is a function of the quantity of carbon picked up by the specimen. This is illustrated by the 1500°F creep data in Figs. 2 and 3. First, note that the creep rate is higher in CO_2 than in CO. Since the carburization rate is higher in CO than in CO_2, this observation is consistent with expectations. It is also important to observe that the creep rates in either environment decrease with time, again indicating a dependence on the carbon concentration. At 1300 and 1700°F the creep-rupture behavior is similar to that just described for 1500°F test conditions.

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[4]R. W. Swindeman and D. A. Douglas, J. Nuclear Materials 1, 49–57 (1959).

Although these data clearly demonstrate the influence of the quantity of carbon present, there are other more subtle factors, the importance of which is not shown. For example, the size and distribution of carbides cannot be overlooked. Garofalo[5] has demonstrated the ability of carbides to retard the movement of dislocations in type 316 stainless steel during creep at 1100, 1300, and 1500°F. Specimens were solution annealed, prestrained, annealed at a 900°F temperature to precipitate the carbides along dislocations, and creep tested in the above temperature range. Enhancement of creep properties was observed as a result of this treatment. However, the amount of prestrain was found to be important since agglomeration occurred at prestrain in excess of 25%. Another factor of possible importance is the change in chemistry of the metal brought about by the formation of carbides. If the carbide formed is $Cr_{23}C_6$, 1.67 wt % Cr will be taken out of solution for every 0.1 wt % C added. The depletion of the matrix in chromium probably increases the solubility of the interstitial elements, O_2, N_2, and C. Work is currently in progress to evaluate these secondary processes.

It is felt that environments which cause nitriding enhance the creep properties through the same mechanisms just discussed for the case of carburization. However, there are some important features as to the conditions under which nitrogen is absorbed. At 1500 and 1700°F nitrides are formed during tests in pure nitrogen (see Figs. 17 and 18). However, at 1500°F nitrides were formed only in areas which underwent deformation. Nitride formation is more general at 1700°F and large quantities of nitrogen are introduced. For example, the specimen shown in Fig. 18 contained 1.20 wt % N_2 after test. The formation of nitrides in specimens tested in air is inhibited by the presence of an oxide film. In fact it was the conclusion of recent studies at Battelle Memorial Institute[6] that 0.5 vol % O_2 in nitrogen is sufficient to completely prevent nitriding of type 318 stainless steel over a 1000-hr period at 1650°F. The results given in Table 4 of a series of tests at

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[5]F. Garofalo et al., Am. Soc. Metals, Qtly. Trans. 54, 430 (1961).

[6]Donald L. Keller (ed.), Corrosion of Stainless Steels in High Temperature Nitrogeneous Environments, BMI-1361 (July 14, 1959).

1700°F in air do not lend support to the findings at Battelle. The photomicrographs of this series of tests in Figs. 11–15 show that the formation of nitrides is a definite function of the strain rate and probably depends also upon the time of exposure. At 1500°F no nitride formation has been observed in specimens tested for as long as 3025 hr in air. However, Dulis and Smith[7] describe a type 304 stainless steel specimen tested in air at 1500°F for 10,000 hr in which nitrides were formed. On the basis of the results just described, it is concluded that the formation of nitrides in type 304 stainless steel tested in air is a function of the strain rate, temperature, and time of exposure. This combination of factors necessary to produce nitriding is that which makes clean surface available to the nitrogen. If the strain rate is not such that reactive metal surface is exposed, extremely long times are required for the nitrogen to permeate or diffuse through the surface oxide.

The influence of oxygen on the creep properties is shown in Figs. 2, 3, and 4. At 1700°F oxygen is strengthening, the mechanism probably being that of internal oxidation. At 1500°F oxygen is somewhat deleterious. In an effort to better understand the influence of oxygen at 1500°F, a series of tests at various oxygen partial pressures were run. The results shown in Figs. 5 and 6 show a marked strengthening at very low oxygen levels and a subsequent reduction in strength at higher oxygen levels. As shown, this difference is manifested through both an influence on the secondary creep rate as well as the rupture life. Figure 7 shows that the crack density increases as the oxygen concentration increases. The results of these tests are currently unexplained since all of the oxygen pressures except the lowest result in surface oxidation. However, they cause one to look upon the mechanism of strengthening by internal oxidation in this material at 1500°F and oxygen pressures near 1 atm with skepticism.

In light of the observations made regarding the behavior of materials in pure oxygen at 1500°F, there is some doubt as to the mechanism responsible for the enhancement of creep properties observed in air at 1500°F.

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[7]E. J. Dulis and G. V. Smith, Trans. Met. Soc. AIME 194, 1083 (1952).

It was pointed out previously that no nitrides were visible in specimens tested in air at 1500°F and the analyses in Table 3 do not indicate a substantial increase in nitrogen. However, these analyses represent the average of a cross section of the specimen and the nitrogen concentration could be relatively high near the surface without raising the average. Hence, it is presently postulated that the observed strengthening in air at 1500°F is due to the influence of nitrogen near the surface on the formation and propagation of cracks. However, at 1700°F oxidation does seem to offer some degree of strengthening and the enhancement of creep properties in air may be a consequence of both nitriding and oxidation.

Oxidation also occurs in CO and CO_2 environments. In light of the tests run in pure oxygen, it is felt that the strengthening observed in CO and CO_2 environments is due primarily to carburization.

At 1500°F the creep properties are essentially the same in argon and hydrogen. However, at 1700°F the creep properties are inferior in hydrogen as compared with those in argon. This is probably due to the removal of carbon by the hydrogen.

Although the addition of carbon improves the creep resistance of type 304 stainless steel, this improvement occurs with reduction in rupture ductility. The tests described in Table 7 and in Fig. 28 do not give a complete picture of the influence of carbon content. However, it is felt that the following generalizations are warranted: (1) The ductility is reduced as the carbon content is increased. (2) The presence of surface layers high in carbon serves as nucleation sites for cracks which propagate across the test piece. Hence, for a given average carbon content, the ductility is higher if the carbon is uniformly distributed.

Although the ductility is not reduced to an alarming level by moderate carbon additions, the problem is worthy of serious consideration. It is conceivable that carbon concentrations in excess of 1 or 2 wt % may result over long periods of use in a carburizing environment. Another reason for concern is that the role of carbon distribution has not been evaluated. Carbon distributions more embrittling in nature than those studied might easily be obtained as a result of mechanical and thermal cycling as might be encountered during the operation of a reactor.

Although moderate carburization does not appear to adversely affect the mechanical behavior of this material, it may be desirable to completely eliminate carburization in some very critical parts. Copper plating seems to be a very good inhibitor for carburization at 1300°F in CO. However, the service life of this coating at higher temperatures is limited.

SUMMARY AND CONCLUSIONS

A study was made of the creep properties of type 304 stainless steel in Ar, CO, CO_2, H_2, N_2, O_2, and air at 1300, 1500, and 1700°F. These studies were made to determine what problems might exist in utilizing this material for capsulating UO_2 fuel in a helium gas-cooled, graphite-moderated reactor containing small amounts of the above gases as contaminants. On the basis of the work completed to date, the following conclusions are made:

Creep properties determined in pure argon are conservative values for design purposes as compared with all environments except hydrogen and possibly pure oxygen.

Air and nitrogen increase the creep resistance of this material at 1500 and 1700°F over that observed in argon. No strengthening was noted in an environment of pure oxygen, suggesting that nitrogen is responsible for the strengthening observed in air.

Carburization occurs in environments of CO and CO_2 at 1300 through 1700°F. Both environments increase the creep resistance.

The ductility is reduced as a result of carburization. The extent of this reduction in ductility is dependent upon the quantity of carbon absorbed by the material and the distribution of the carbon.

Copper plating is effective at 1300°F in decreasing the carburization rate of this material under stress in a CO environment. The service life of copper coatings is seriously limited at temperatures in excess of 1300°F.

Although no testing experience has been obtained in environments comparable with those which will be present in the Experimental Gas-Cooled Reactor, this work makes possible some general remarks about the use of type 304 stainless steel in this application. Because of the very low

impurity levels required to oxidize type 304 stainless steel, oxidation will occur. The extent of the damage caused by this process alone will depend upon the metal temperature and the gas composition. Gas mixtures rich in CO_2 tend to result in the formation of Fe_3O_4 which spalls readily upon thermal cycling. Other mixtures, particularly those high in CO, cause spinels to be formed which are more protective and more adherent. The presence of oxide particles in the gas stream, as well as the resultant embrittlement and loss of metal due to oxidation, are potential problems. Carburization will also most likely occur as a result of exposure to the EGCR environment. The potential problem here is embrittlement due to increased carbon content. Data have been presented in this paper which show that quite high carbon concentrations can be tolerated. However, there are several unanswered problems relative to the distribution of carbon. For example, adding carbon at high temperatures and reprecipitating at lower temperatures is shown to be bad by the work reported by Garofalo.[5] Hence, when possible, fuel elements should be repositioned to higher operating temperatures, not lower. The last comment is relative to the misconception that the impurities should be held as low as possible. There are numerous opposing reactions which are occurring in a system of this nature and many concentration ratios are important. Hence, the operating conditions should be those which minimize for the largest number of elements the rates of gas-metal reactions known to be harmful. This may even require the addition of an impurity. However, sufficient experimental data are not presently available to utilize this concept to its fullest advantage.

ACKNOWLEDGMENT

The authors would like to acknowledge the able assistance of several service groups at the Oak Ridge National Laboratory in carrying out this research and in preparing this paper: the Analytical Chemistry Division, the Graphic Arts Department, and the Metallography and the Reports Office groups of the Metals and Ceramics Division. The mechanical

property tests were conducted by E. Bolling, J. East, V. G. Lane, and C. Dollins. Annealing and metal compatibility tests were conducted by B. McNabb and K. W. Boling. The assistance through consultation of co-workers W. R. Martin and J. R. Weir is gratefully acknowledged.

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