The Effects of Deformation Induced Martensite on the Sensitization of Austenitic Stainless Steels

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This paper compares the effects of deformation which induces martensite in austenitic stainless steel with deformation which does not on the sensitization and corrosion susceptibility of these alloys. We show that deformation which induces martensite causes rapid sensitization at temperatures below 600 °C, leads to extensive transgranular corrosion, and can produce rapid healing. The martensite is also an area of extensive carbide precipitation. Deformation alone noticeably increases the kinetics of sensitization only at temperatures where undeformed samples are readily sensitized. Without the presence of martensite, intergranular corrosion is always the predominant corrosion path, rapid healing is not observed, and most carbides precipitate along the grain boundaries.

INTRODUCTION

THE fact that certain heat treatments make nonstabilized austenitic stainless steels susceptible to corrosion greatly limits the applications of these alloys. The heat treatments which produce this susceptibility or sensitization involve isothermally heating in, or slowly cooling through, the range 600 to 800 °C. The corrosion which results is most often intergranular. Its occurrence has been attributed to the precipitation of chromium carbides along the grain boundaries during these sensitizing heat treatments and the concomitant depletion of chromium around the growing carbide.[1] This chromium depletion model gains support from the facts that intergranular chromium carbides do form during sensitizing heat treatments, that lowering the chromium content makes the steel more susceptible to corrosion, and that long time heat treatments in the sensitizing temperature range do restore the excellent corrosion properties to the material. This latter phenomenon is called healing and presumably occurs because chromium has sufficient time to diffuse to the depleted boundary.

Throughout the years examples have shown that prior cold work changes the sensitization process. Bain and co-workers[1] showed that cold work led to rapid healing. They suggested that this rapid healing occurred because the carbides could nucleate both along the grain boundaries as well as along the slip bands within the grains. With the higher density of carbides, less chromium depletion would occur at any point. Tedmon, Vermilyea, and Broecker[2] found that cold work produced rapid healing in 304 stainless steel if applied before sensitization, but increased the corrosion rate if applied after sensitization. They suggested that this increase could result from rapid corrosion of the martensite which formed during the deformation.

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Manuscript submitted May 13, 1980.

Other workers[3–9] have specifically studied the effects of deformation induced martensite on the corrosion of 304 stainless steel. Several[3–5] have found that its presence increased both the corrosion rate of samples held potentiostatically in the active range and the critical current density required for passivation. Vermilyea[6] showed that austenitic steels containing martensite were more susceptible to stress corrosion cracking in aqueous solutions than were solution annealed samples, and Honkasalo, *et al*[7] found that the martensite was preferentially corroded in U-bend tests in sulfate solutions. Finally, Hahin and co-workers[8] reported that deformation by cold upset forging of sensitized samples greatly increased the corrosion rates of type 304 and 304L stainless steel in the highly oxidizing Huey test once the deformation was sufficient to induce martensite. Deformation did not increase the corrosion of 316 stainless steel, nor did it induce martensite in the alloy.

Recently, we showed that deformation prior to sensitization could greatly accelerate the kinetics of sensitization in a type 304 stainless steel.[9] For example, a sample which had been pulled in tension to 344.7 MN/m^2 (50 KSI) was attacked in the modified Strauss test (ASTM A262E) after a heat treatment of 30 min at 500 °C. An undeformed sample required over 100 h of heat treating at this temperature to produce a microstructure susceptible to corrosion in the same test. Furthermore, we found that the deformed samples corroded primarily along a transgranular path, while corrosion in the undeformed samples was completely intergranular. Transmission electron microscopy showed that intragranular carbides precipitated in the deformed samples and were always within the deformation induced martensite or along the martensite lath boundaries. We thus suggested that this rapid sensitization resulted from the fact that chromium and carbon diffuse more rapidly in the body-centered-tetragonal martensite than in the face-centered-cubic austenite. This would speed up the onset not only of sensitization but also of healing.

One problem which earlier work[1–9] did not address was the separate effects of prior cold work and of martensite on the sensitization of austenitic stainless steels. We know that cold work alone produces exten-

ISSN 0360-2133/80/1211-2009$00.75/0

sive dislocation networks which could allow rapid pipe diffusion of the chromium and carbon.[10] Also, the cold work could enhance nucleation of chromium carbides, and the slip bands produced during deformation could provide nucleation sites for intragranular carbides.[11] In this paper we show that if the cold work induces martensite it has a much greater effect on the subsequent sensitization of the alloy than if it does not. We do this by comparing the effects of deformation on the sensitization of 304 and 316 stainless steel. Deformation produces martensite in the 304 stainless steel but not in the 316 stainless steel. We will show that the rapid sensitization at low temperatures, the occurrence of extensive transgranular corrosion, and the rapid healing primarily result from the presence of martensite and not just cold work.

EXPERIMENTAL

Commercial alloys were used for this study. The chemical compositions are given in Table I. The alloys were purchased as rod with a diameter of 0.3175 cm.

All samples were initially given a solution anneal heat treatment of 1 h at 1100 °C, followed by a water quench. Some samples were then isothermally aged to determine the sensitization characteristics of the undeformed material. Other samples were first deformed and then aged. Aging heat treatments were isothermal and were followed by a water quench. An argon atmosphere was used for all heat treatments.

Deformation was introduced by pulling the samples in tension. After the solution anneal heat treatment a gage section of 0.254 cm diam was electropolished into the samples. This method avoided any excess surface deformation which could uncontrollably affect our results. The type 316 samples were pulled to 582.6 MN/m^2; the load was then released. The type 304 samples were pulled to 643.1 MN/m^2 followed by a load release. The two stresses were chosen because they are 34.5 MN/m^2 or 5 KSI below the maximum tensile stress that these alloys can withstand.

Sensitization was monitored with the modified Strauss test (A262E).[12] Prior to this test all samples received a final electropolish and ultrasonic cleaning. This facilitated examination of the corrosive attack after the test. In this test samples are placed in a boiling aqueous solution of sulfuric acid and copper sulfate for three days. During the test the samples are wound with copper wire and surrounded by copper chips. After the test the samples are removed, bent into a U-shape, and inspected for corrosive attack. The results of these tests were described in one of three ways. No attack meant that no corrosive attack could be observed at a magnification of 250 times. Partial attack meant that corrosion had occurred but that the sample remained in one piece upon bending. Failure meant that the sample broke into two pieces when bent. Throughout this paper a sample will be defined as sensitized if this test produced any attack at all.

Table I. Chemical Compositions of Steels

	C	Mn	Ni	Cr	P	S	Si	Mo	Cu	Fe
Type 316	0.057	1.67	12.77	17.14	0.035	0.025	0.54	2.21	0.31	Bal
Type 304	0.078	1.12	8.49	18.1	0.025	0.027	0.41	—	0.21	Bal

RESULTS

Fig. 1 shows the behavior of undeformed samples of these two alloys of stainless steel in the modified Strauss test after various aging heat treatments. In these two plots each point represents the time and temperature of the heat treatment. The symbol denotes the corrosion behavior in the modified Strauss test of a sample given that heat treatment, and the dashed line separates the region in the graph of time-temperature combinations that produced sensitization and those that did not. We see that the corrosion behavior of the two alloys is quite similar. The corrosion always proceeded along an intergranular path, Fig. 2, and in sensitized samples chromium carbides ($M_{23}C_6$) had precipitated along the grain boundaries, Fig. 3. The growth of these carbides creates a chromium depleted region at the grain boundaries and causes intergranular corrosion in the modified Strauss test.

Samples which were deformed in tension but not given any additional aging heat treatment were not attacked in the modified Strauss test. However, both transmission electron microscopy and the ferrofluid metallographic technique[13] showed that this deforma-

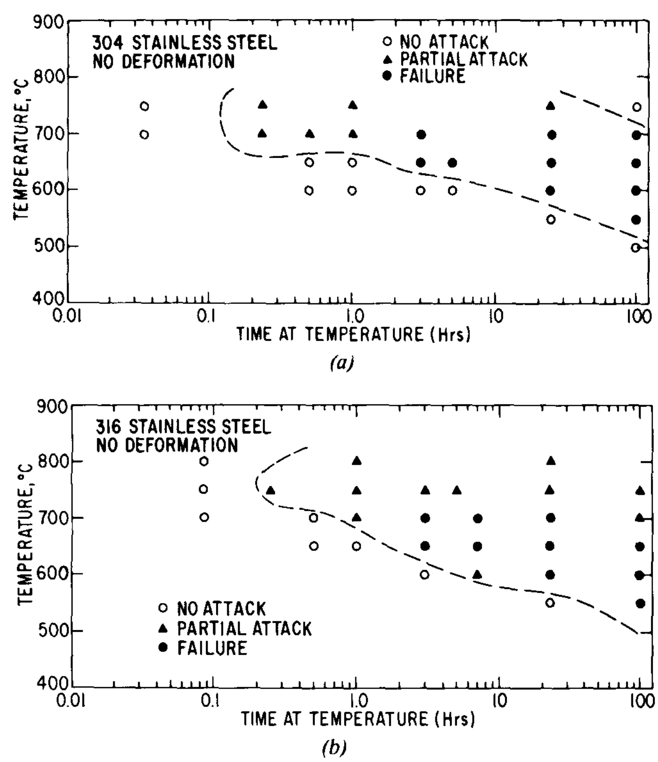


Fig. 1—The results of the modified Strauss test for undeformed samples of the two types of alloys. Each point is for a time and temperature of heat treating. Each symbol denotes the response in the test. (*a*) 304 stainless steel, (*b*) 316 stainless steel. The dashed lines separate the time-temperature combinations which produce sensitization from those that do not.

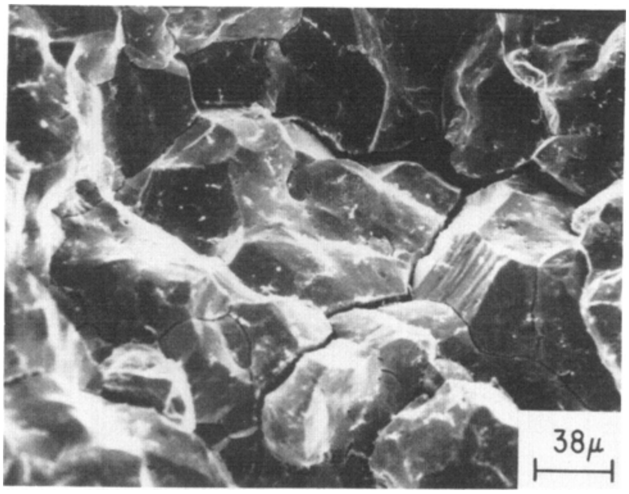
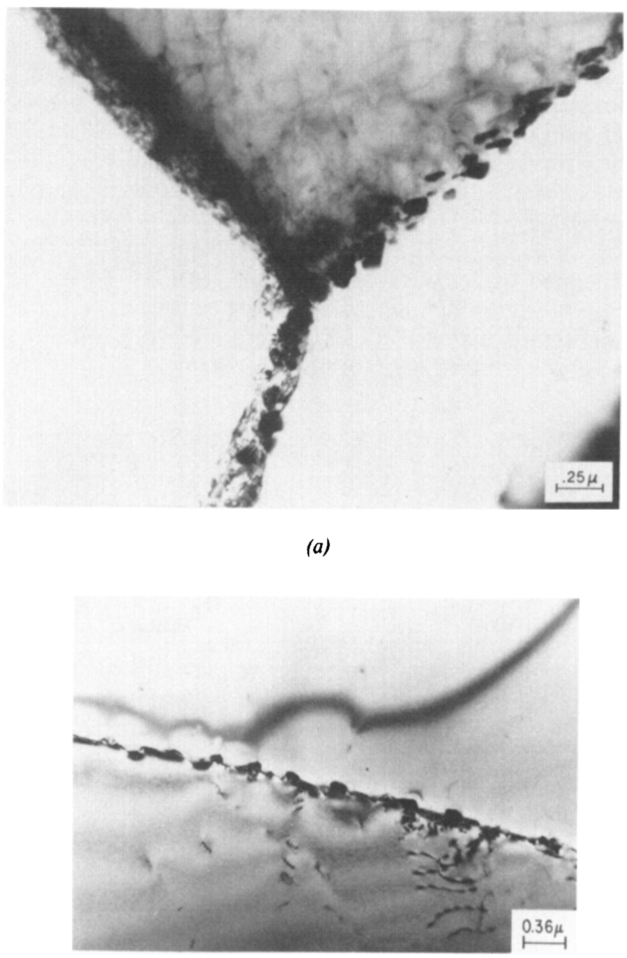


Fig. 2—Intergranular corrosion of an undeformed sample in the modified Strauss test. This micrograph is of a sample of the 316 alloy.



(a)

(b)

Fig. 3—Transmission electron microscopy showing the grain boundary carbides present in sensitized samples of the undeformed alloy. The carbides were indexed as $M_{23}C_6$. (*a*) 304 stainless steel, (*b*) 316 stainless steel.

tion had produced martensite in the 304 stainless steel but not in the 316 stainless steel.

Fig. 4 shows the corrosion behavior of the deformed samples after aging heat treatments. Table II compares the minimum aging time at a given temperature required to cause partial attack in both deformed and undeformed samples in the modified Strauss test.* It is clear from Table II and Figs. 1 and 4 that deformation influences the sensitization behavior of these two alloys differently. First, let us consider the type 316 alloy.

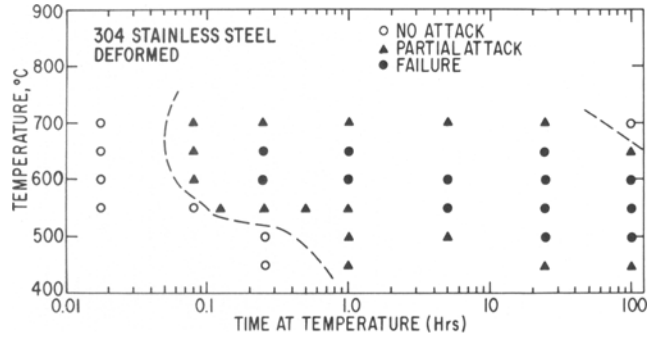
At 500 and 450 °C, heat treatments of 100 h or less did not produce a sensitized microstructure in either the deformed or undeformed steels. As the temperature increased, the effects of deformation became more pronounced. At 600 °C, 0.5 to 1 h produced a sensitized microstructure in deformed samples; 3 to 7 h were required for undeformed samples. Similarly, a heat treatment of 15 min at 650 °C sensitized a deformed sample, whereas 1 to 3 h were needed to sensitize undeformed samples. At 750 °C both deformed and undeformed samples are readily sensitized but never to the extent that they break into two pieces upon bending (*i.e.*, failure in Figs. 1 and 4). Also, 100 h at 700 °C causes both deformed and undeformed samples not to be corroded to failure in this test. They are therefore partially healed, since shorter times at this temperature did cause complete failures.

Heat treating deformed 304 stainless steel at 450 and 500 °C for 1 h produced a sensitized microstructure. At 550 °C, ten min of heat treating caused sensitization, and at 600 and 650 °C five min were needed. This sensitization is much more rapid than that observed in the undeformed samples, especially at temperatures of 550 °C and below. Deformed samples heat treated for 100h at 650 °C and at times from 5 min to 24 h at 700 °C were only partially attacked. A sample heat treated for 100 h at 700 °C was not attacked. We note that samples given heat treatments of 100 h at 650 °C or 3 to 100 h at 700 °C were only partially attacked or completely unattacked in the gauge section. The undeformed grips failed the modified Strauss test, Fig. 5. Therefore, the deformation which induced martensite has given rise to more rapid healing than is observed in the undeformed sample.

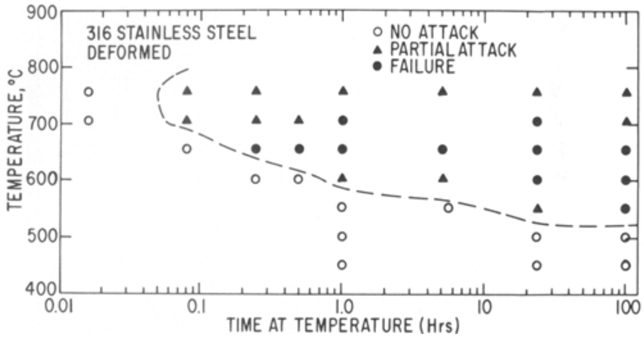
*Throughout the text and in Tables II and III the ranges of time given for the minimum time required for sensitization are the longest heat treatment time that did not cause attack in the modified Strauss test and the shortest time that did at any given temperature.

Table II. Minimum Time Required for Attack in Modified Strauss Test

	316		304	
Temperature (°C)	No Deformation (H)	Deformation (H)	No Deformation (H)	Deformation (H)
450	>100	>100	>100	0.25–1.0
500	>100	>100	>100	0.25–1.0
550	24–100	5–24	24–100	0.08–0.12
600	3–7	0.5–1.0	5–24	0.016–0.08
650	1–3	0.08–0.25	1–3	0.016–0.08
700	0.5–1.0	0.016–0.08	0.035–0.25	0.016–0.08



(a)



(b)

Fig. 4—The results of the modified Strauss test for deformed samples of these alloys. (*a*) 304 stainless steel and (*b*) 316 stainless steel. The dashed lines separate the time-temperature combinations that produce sensitization from those that do not.

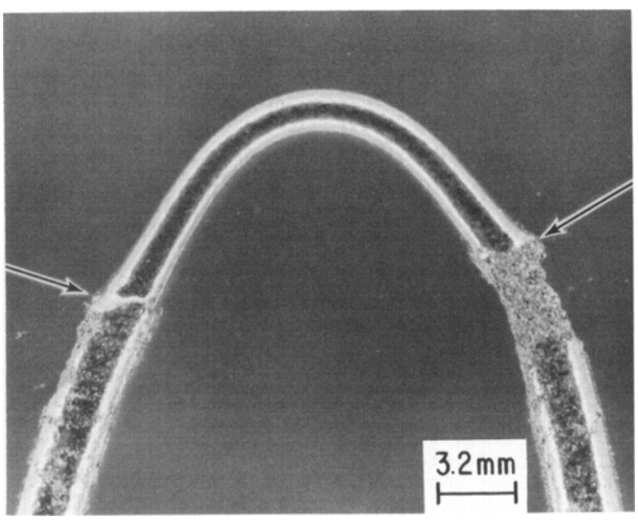


Fig. 5—An optical micrograph of 304 stainless steel after the modified Strauss test. The sample had been heat treated for 100 h at 700 °C. Note that the martensite containing gauge section is completely healed whereas the undeformed grips are badly corroded. Arrows denote the end of the gauge section and start of the grips.

The path of corrosive attack in deformed samples of the two alloys differed. The attack on lightly sensitized samples of 316 stainless steel was completely intergranular, Fig. 6(*a*). Only after longer heat treatments was transgranular attack also observed, Fig. 6(*b-d*). The time required for the onset of transgranular corrosion decreased as the temperature increased. The observed transgranular attack in this alloy was always in addition to complete intergranular attack and not in lieu of it. Therefore, samples which contained transgranular corrosion opened along the grain boundaries and the attack could be seen penetrating from the boundary into the grain or from the surface into the grain.

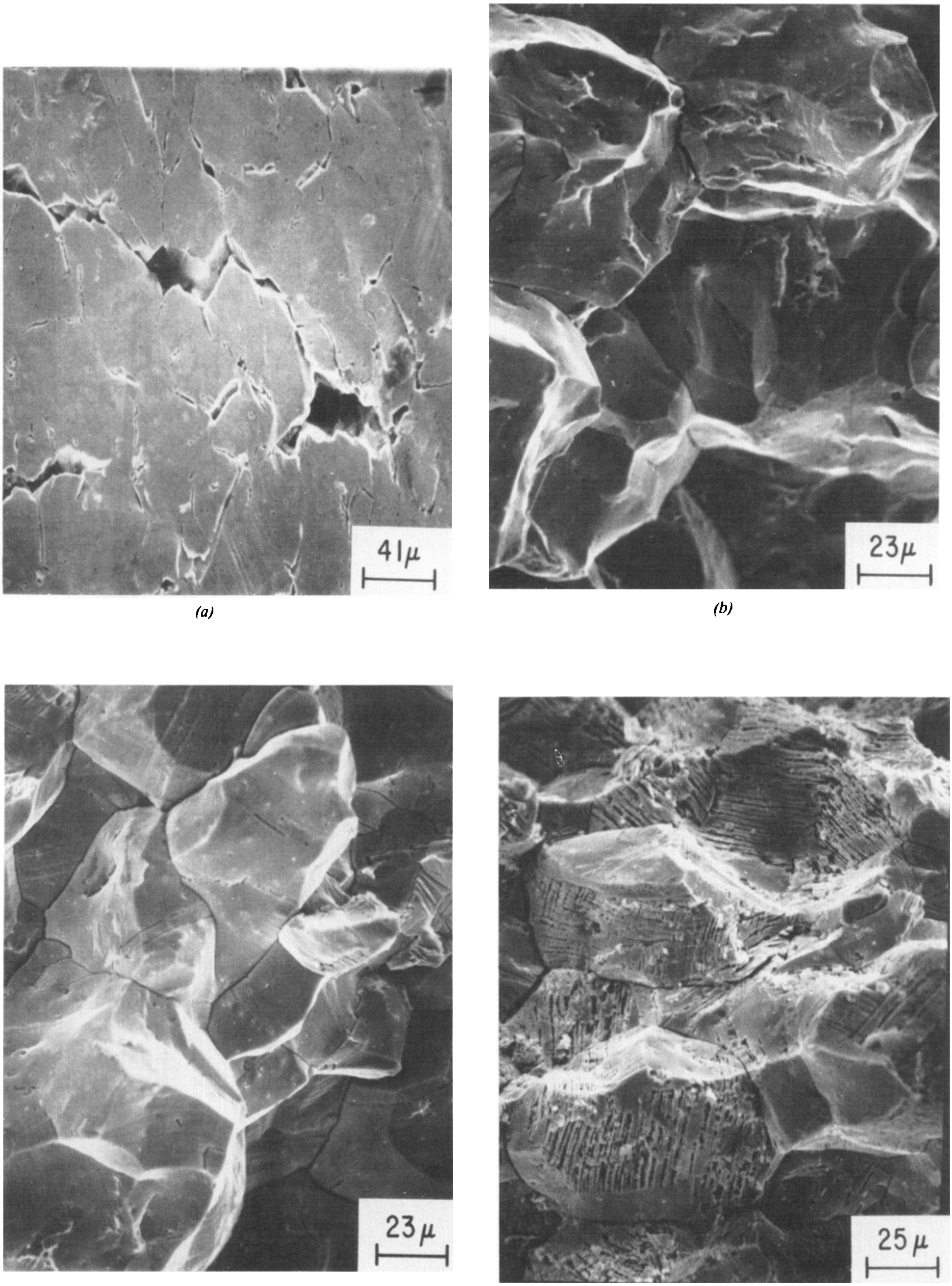
The corrosion of deformed samples of type 304 stainless steel sensitized at 450 and 500 °C was completely transgranular with no accompanying intergranular attack, Fig. 7(*a*) and (*b*). Sensitization at times less than 24 h at 550 °C caused transgranular corrosion, but after 24 and 100 h aging treatments some intergranular attack was also observed. Corrosion of all samples sensitized at 600 °C and above contained both intergranular and transgranular components, Fig. 7(*c*) and (*d*). Most of these samples which failed the modified Strauss test broke apart along the grain boundaries, but the individual grains contained extensive transgranular corrosion, Fig. 7(*e*).

The location of the carbides in the deformed samples also differed between the two alloys. In the 316 stainless steel the carbides initially precipitated along the grain boundaries, and after all sensitizing treatments most carbides were found there. However, with sufficient time carbides did precipitate slip planes and twin boundaries, Fig. 8. In the 304 stainless steel many intragranular carbides were found and these were always within martensite laths or along the lath boundaries. During aging treatments below 600 °C, most carbides which formed were intragranular and associated with the martensite, Fig. 9(*a*). At temperatures which would normally sensitize undeformed material, both intergranular and intragranular carbides were found, Fig. 9(*b*).

DISCUSSION AND CONCLUSIONS

This work compares the effects of deformation which does not induce martensite with deformation which does on the sensitization of austenitic stainless steels. To accomplish this goal we have determined the effect of deformation on the sensitization of a type 316 and a type 304 stainless steel. In the undeformed state the steels have remarkably similar sensitization kinetics, and the sensitized samples corrode intergranularly. However, deforming the samples to within 34.5 MN/m^2 of their maximum tensile stress produces martensite in the type 304 alloy but does not in the type 316 alloy. The presence or absence of martensite leads to quite different sensitization behavior. These differences can be summarized and explained in the following way.

Deformation reduces the times required for sensitization. However, the effect is much greater in the martensite containing 304 stainless steel than in the type 316 stainless steel, especially at temperatures below 600 °C. Table III emphasizes this fact. These low temperatures are out of the normal rapid sensitization range of most austenitic alloys. The very rapid sensitization of the type 304 stainless steel results directly from the presence of the martensite. Because chromium and carbon can diffuse more rapidly in the body-centered-tetragonal martensite

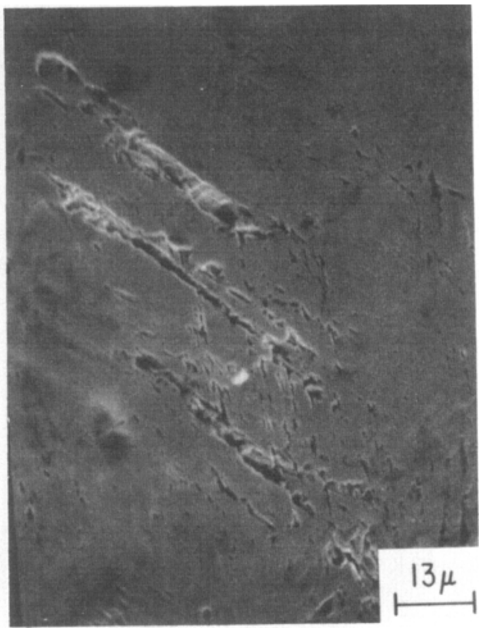


(a) (b) (c) (d)

Fig. 6—Corrosion attack on deformed and sensitized 316 stainless steel. (*a*) A sample partially attacked after heat treating. This shows that the initial attack was always intergranular in lightly sensitized samples. (*b*) through (*d*) show that the amount of transgranular attack increased as aging time at a given temperature increased. Fig. (*b*) shows a sample aged for 0.25 h at 650 °C, (*c*) shows a sample aged 1 h at 650 °C, and (*d*) shows a sample aged 24 h at 650 °C.

Table III. Minimum Time at Temperature Required for Attack in Modified Strauss Test

Temperature	Time (H)	
(°C)	Cold Worked 316	Cold Worked 304
450	>100	0.25–1.0
500	>100	0.25–1.0
550	5–24	0.08–0.12
600	0.5–1.0	0.016–0.08
650	0.08–0.25	0.016–0.08
700	0.016–0.08	0.016–0.08



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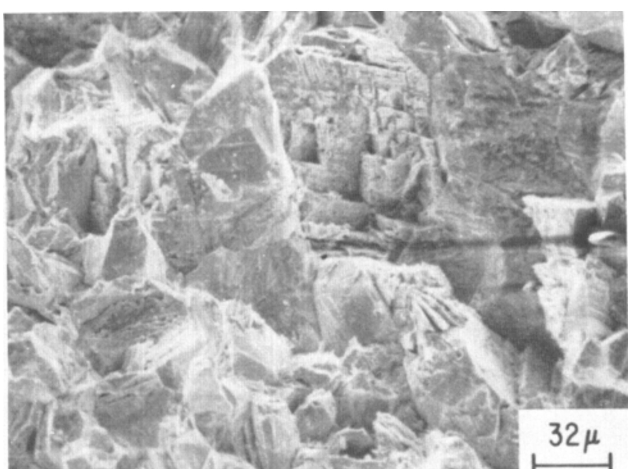

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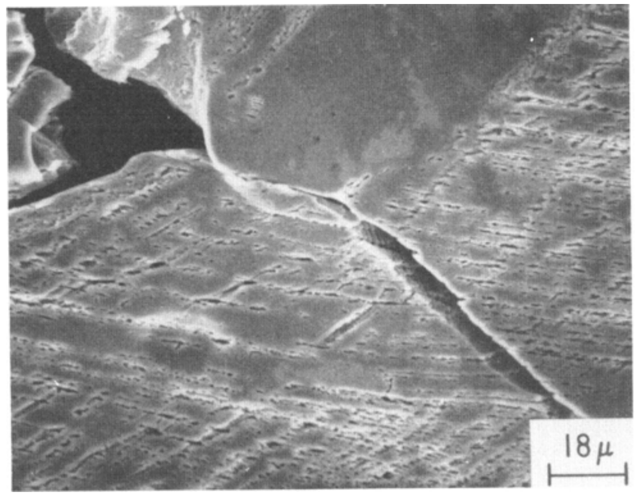

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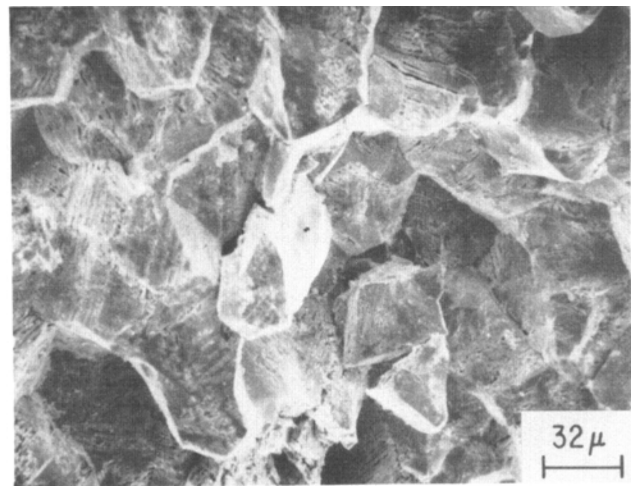

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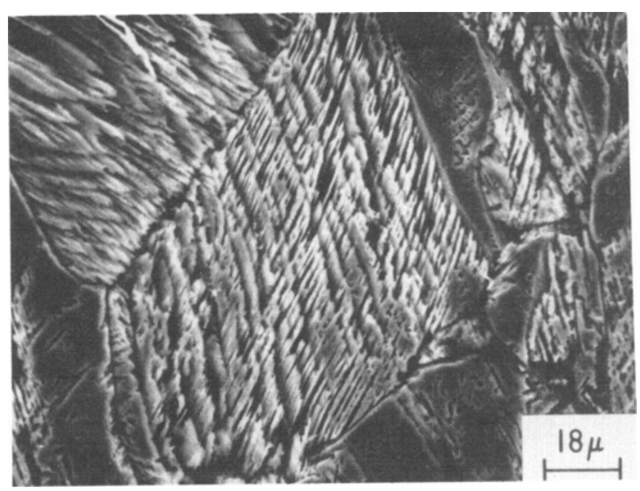


(e)

Fig. 7—Corrosive attack in deformed and sensitized 304 stainless steel. (*a*) This figure shows that initial attack was always transgranular. The sample was sensitized at 450 °C for 24 h. (*b*) Complete failure in the modified Strauss test of a sample sensitized at 500 °C for 24 h. Note that the failure is completely transgranular. Figure (*c*) shows a sample sensitized at 650 °C for 5 min. Note both transgranular and intergranular attack. Fig. (*d*) shows an example of a sample that broke apart along the grain boundaries but contained extensive transgranular corrosion. Fig. (*e*) shows a high magnification of the transgranular corrosion.

than in the face-centered-cubic austenite,[14] precipitation of chromium carbides can occur at lower temperatures. Transmission electron microscopy has shown that the chromium carbides do form at these temperatures and are associated with the martensite laths, Fig. 9. These intragranular carbides produced the transgranular corrosion shown in Fig. 7. No car-

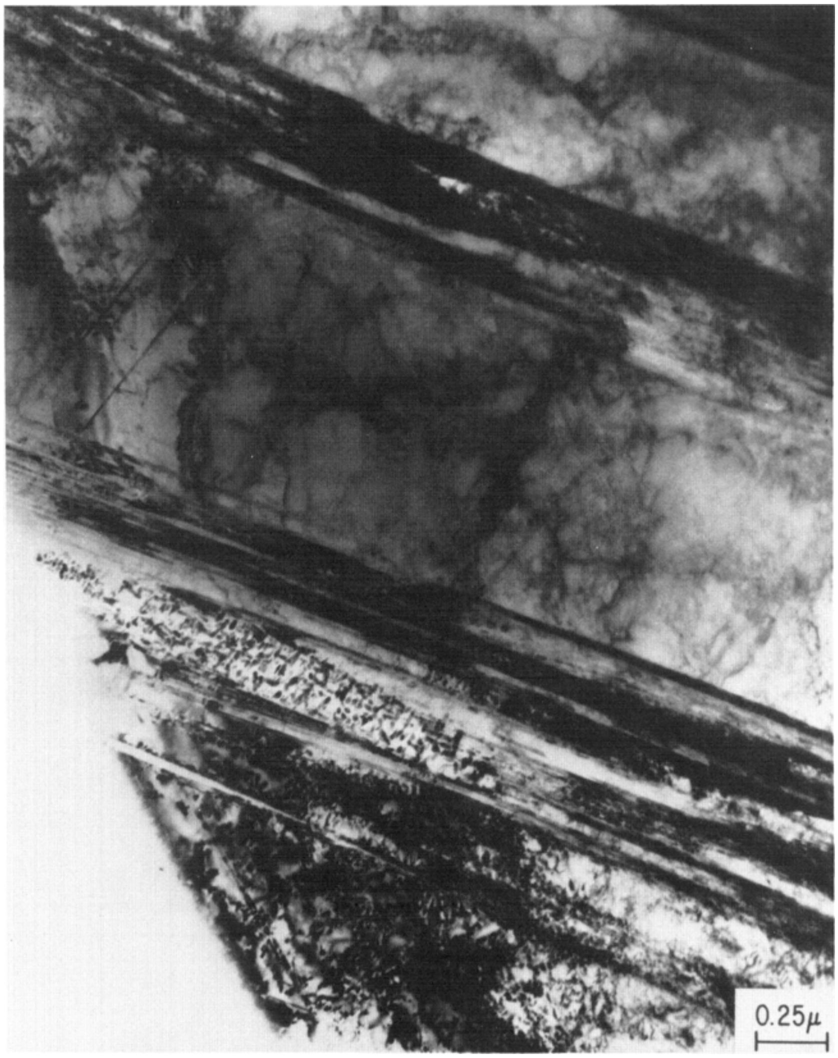
Fig. 8—A transmission electron micrograph of a deformed and sensitized 316 stainless steel sample. The sample was sensitized after deformation at 650 °C for 100 h. The carbides shown are precipitated at a twin boundary, as indicated by the arrows.

bides or corrosion were observed in the deformed 316 samples after aging at these low temperatures.

At temperatures of 600 and 650 °C, sensitization occurs rapidly in undeformed alloys. Deformation increased the kinetics of sensitization in both alloys, and the times required for sensitization in either alloy are similar. However, samples of the 316 alloy sensitized for short times corroded intergranularly and only with continued sensitization did transgranular corrosion accompany the intergranular corrosion. Deformed samples of the 304 steel heat treated for short times at these temperatures corroded both intergranularly and transgranularly. This difference in corrosion between the two types of alloy can be seen in Fig. 10, which compares attack in modified Strauss test of samples of each alloy heat treated for 15 min at 650 °C. In the type 316 steel only intergranular corrosion is observed, as opposed to both intergranular and transgranular corrosion in the 304 sample.

In both alloys any transgranular corrosion which occured after heat treatments in this temperature range (600 to 650 °C) could be associated with intragranular carbides. However, in the 304 stainless steel carbides can nucleate easily both at the grain boundaries and in the martensite. This leads to a very high density of carbides. In the 316 stainless steel, the grain boundaries remain the preferred location for carbide precipitation. Only with time do intragranular carbides form.

The deformed 316 stainless steel samples sensitize readily at 700 °C and after heat treatments of 3 to 24 h exhibit failure in the modified Strauss test. However, samples of 304 stainless steel were either partially attacked or completely healed after heat treatments at 700 °C. This behavior contrasts not only with that of the deformed 316 stainless steels but also with the undeformed 304 stainless steel. This rapid healing again results from the presence of martensite. Even at very short time heat treatments at 650 and 700 °C many carbides precipitate at the grain boundaries as well as within the martensite. This high density means that chromium depletion around any carbide will never be as great. Furthermore, the martensite is especially efficient at precipitating carbides because the solubility of carbon is lower in the martensite than in the austenite.[15] This means that most of the carbon



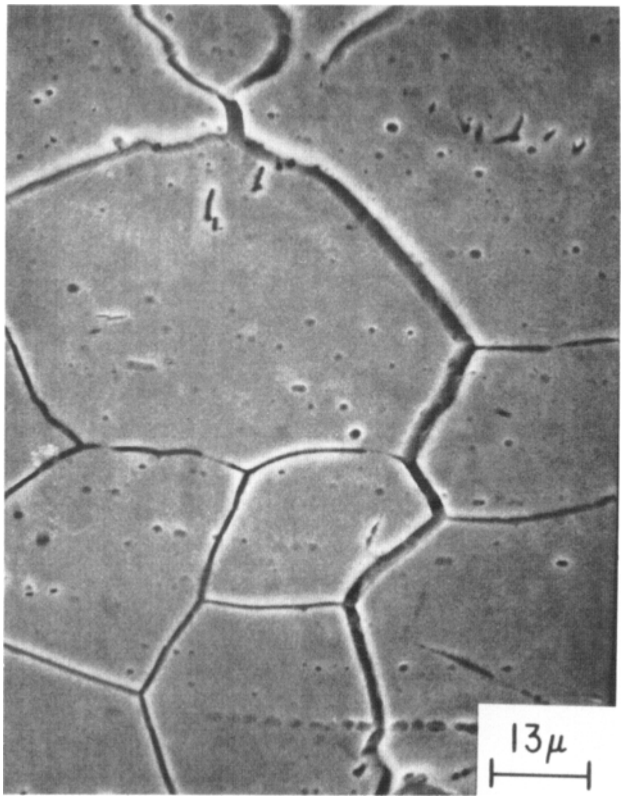
(a)

(b)

Fig. 9—(a) A transmission electron micrograph of a sample of 304 stainless steel that was first deformed and then sensitized for 1 h at 550 °C. Note the carbides in the martensite laths. (b) An optical micrograph showing the presence of intergranular and intragranular carbides in a sample of deformed 304 stainless steel heat treated for 24 h at 700 °C.

in the martensite rapidly goes into the formation of carbides,[16] giving a high density of fine carbides.

In summary, we conclude that martensite affects the sensitization of austenitic stainless steels in the following unique ways. It produces very rapid sensitization at temperatures below 600 °C, it causes extensive transgranular corrosion, it can lead to rapid healing, and it is a site of extensive carbide precipita-



(a)

(b)

Fig. 10—A comparison between attack in deformed (*a*) 316 stainless steel and (*b*) 304 stainless steel after a heat treatment of 650 °C for 0.25 h. Note that attack in the 316 sample is completely intergranular whereas in 304 extensive transgranular attack has occurred.

tion. Cold work alone noticeably increases the kinetics of sensitization only in the temperature range where the undeformed samples are also rapidly sensitized. It does not cause extensive transgranular corrosion, it does not lead to rapid healing, and the grain boundaries remain the preferred site for carbide precipitation.

ACKNOWLEDGMENTS

The authors wish to thank D. N. Wemple for his technical assistance throughout the course of this work. This work was supported by the Electric Power Research Institute Contract RP 1574-1.

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