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Hydrogen-assisted cracking of sensitized 316L stainless steel

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Thin tensile specimens of 316L-type austenitic stainless steel were tested either at room temperature after cathodic charging or whilst undergoing cathodic charging. Throughout this study we have compared solution-annealed samples with samples given the additional sensitization treatment. The results of the tensile tests show that the room temperature yield and ultimate strengths were not much affected by sensitization, whilst significant reduction in the ductility was observed depending on the heat treatment and the method of charging. The specimens tested while undergoing cathodic charging showed 21% reduction of elongation at-fracture for the annealed specimens and 49% reduction of elongation for the sensitized specimens. The fracture surfaces of the specimens tested while cathodically charged show considerable differences between the annealed and the sensitized specimens. The sensitized specimens were predominantly intergranular, while the fracture of annealed specimens showed massive regions of microvoid coalescence producing ductile rupture. The results were correlated with the presence or absence of the martensite phases determined by means of a ferrite detector and transmission electron microscopy studies.

1. Introduction

In recent years there have been many studies of hydrogen-assisted cracking in stainless steels [1–8]. Despite many previous studies the determined factor which controls the hydrogen cracking susceptibility of austenitic stainless steels has remained unclear. A problem which has received considerable attention during the past few years has been the effect of sensitization on the hydrogen cracking susceptibility of austenitic stainless steels [6, 7, 9–11].

The phenomenon of sensitization has been reviewed extensively by others [12]. Briefly, an alloy is said to be "sensitized" if it is more susceptible to intergranular attack than a non-sensitized sample of the same alloy. This sensitized condition is usually the result of thermal exposure in the 500 to 800° C temperature range. The most widely accepted explanation for sensitization is the chromium depletion theory of Bain, Aborn and Rutherford [13] which attributed the increased susceptibility to the formation of chromium carbide particles along grain boundaries, and the accompanying depletion of chromium from the adjacent austenite matrix.

Thompson [9] examined sensitization in 309S stainless steel and found that it did not change the mechanical properties of this material in hydrogen, although highly sensitized material did show a decreased dimple size. Fidelle and co-workers [10, 11] found that sensitized 304 stainless steel failed intergranularly when the grain boundary carbides were continuous. Briant [6] reported that sensitized 304 stainless steel failed intergranularly in hydrogen even though the carbides were not continuous along the grain boundaries. No detailed observations of hydrogen-assisted cracking of sensitized 316L stainless steel is available at present.

In this paper we have compared solution-annealed samples with samples given the additional sensitization heat treatment. An attempt was made to corrolate the tensile properties of the hydrogen charged thin specimens with their mode

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TABLE I Chemical composition of 316L stainless steel

Element (wt%)										
Cr	Ni	Mo	Mn	Si	Co	Cu	N	P	C	S
17.65	11.10	2.08	1.80	0.50	0.35	0.21	0.061	0.03	0.026	0.009

of fracture. The martensite formation was detected in connection with the susceptibility of the steel to hydrogen cracking.

2. Experimental procedure

The studies were carried out on a 316L-type austenitic stainless steel. The steel was commercial grade, of the composition shown in Table I, and was received in the form of sheets 0.2 mm thick. Tensile specimens were prepared according to [14]. All of the samples used in these experiments were first solution annealed for one hour at 1100° C and then water quenched. Some samples were given a further heat treatment of 650° C for 24 h. This latter heat treatment should allow the precipitation of chromium carbides along grain boundaries. The samples were cathodically charged with hydrogen at room temperature in a 1 N H_2SO_4 solution with 0.25 g of $NaAsO_2$ per litre, added as an H recombination poison. A platinum counter electrode and a current density of 50 mA cm^{-2} were used. In the electrolytic charging process the hydrogen is liberated at the cathode surface and may diffuse into the sample interior. The impressed voltage driving the cell reaction provides a huge hydrogen fugacity and thus large amounts of hydrogen may be driven into the specimen. The charging process is regarded as a tool by which the effect of hydrogen on mechanical properties may be studied.

The following series of tests were conducted on each steel:

(a) Tensile specimens were tested at an extension rate of 0.005 cm min^{-1}, after cathodic charging in the absence of external stress. The tensile test started within 5 minutes of completion of the cathodic charging.

(b) Specimens were tensile tested at an extension rate of 0.005 cm min^{-1}, while undergoing cathodic polarization.

(c) For purposes of comparison, specimens were tensile tested in air at room temperature.

After failure the fracture surfaces were examined with a scanning electron microscope. A measure of the amount of α-martensite present at the fracture surfaces was obtained using a commercial ferrite detector with a sensitivity of 0.1 vol% α-martensite. Hydrogen effects on the martensitic transformation of the austenite phase to α- or ϵ-phases have been studied using transmission electron microscopy.

3. Results and discussion

Table II summarizes the results for the various heat treatments and testing conditions. A significant feature of the results is that the yield and ultimate strengths were not much affected by sensitization, while significant changes in the ductility of the steel was observed. As can be seen from Table II, stressing at room temperature after cathodic charging resulted in an 8% reduction of elongation-at-fracture for the annealed specimen and a 21% reduction of elongation-at-fracture for the sensitized specimens. The specimens tested while undergoing cathodic charging showed a slight reduction in ultimate strength and a 21% reduction of elongation for the annealed specimens and a 49% reduction of elongation for the sensitized specimens.

Examination of the fracture surfaces of the annealed specimens that were cathodically charged for 15 days and tensile tested in air, shows massive regions of microvoid coalescence producing ductile rupture (Fig. 1b). The sizes of the dimples

TABLE II Per cent reduction in tensile properties of charged specimens as compared to those of uncharged specimens

Heat treatment	Method of testing					
	Tensile testing in air after cathodic charging for 15 days			Tensile testing while undergoing cathodic charging		
	Yield strength	Ultimate tensile strength	Elongation	Yield strength	Ultimate tensile strength	Elongation
Annealed	None	None	8	None	5	21
Sensitized	None	None	21	None	10	49

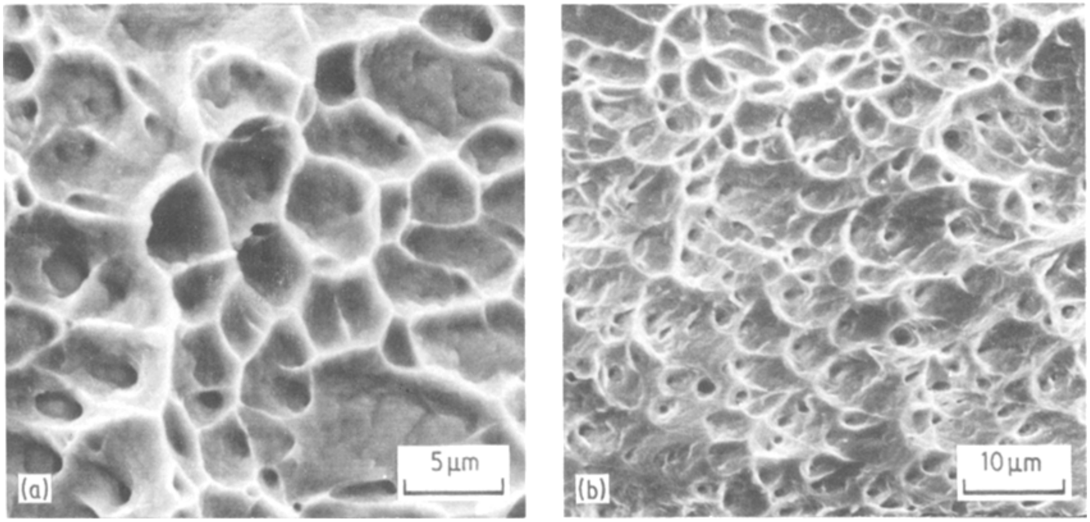

Figure 1 Scanning electron micrographs of fracture surfaces of annealed steel specimens: (a) tested in air; (b) tested in air after 15 days of cathodic charging.

are considerably reduced compared to those for the annealed specimens tested in air at room temperature (Fig. 1a). The annealed fracture specimens that were tested during cathodic charging show a ductile fracture mode of microvoid coalescence similar to that shown in Fig. 1b.

Typical fracture surfaces of the sensitized specimens after cathodic charging for 15 days are shown in Fig. 2a. The initial hydrogen fracture was predominantly intergranular and some regions of microvoid coalescence were observed. The specimens which were tested while cathodically charged show considerable differences in the fracture surfaces between the annealed and the sensitized specimens. The sensitized specimens showed a predominantly intergranular fracture surface (Fig. 2b), while the annealed specimens showed evidence of microvoid coalescence producing ductile rupture, as previously described.

It is now recognized that severe hydrogen embrittlement need not result from microscopic mechanisms which lead to brittle fracture features, such as intergranular cracking and cleavage [15, 16]. As much as 50% reduction in area has been observed in tensile tests of austenitic alloys such as stainless steels [17] without a change in the

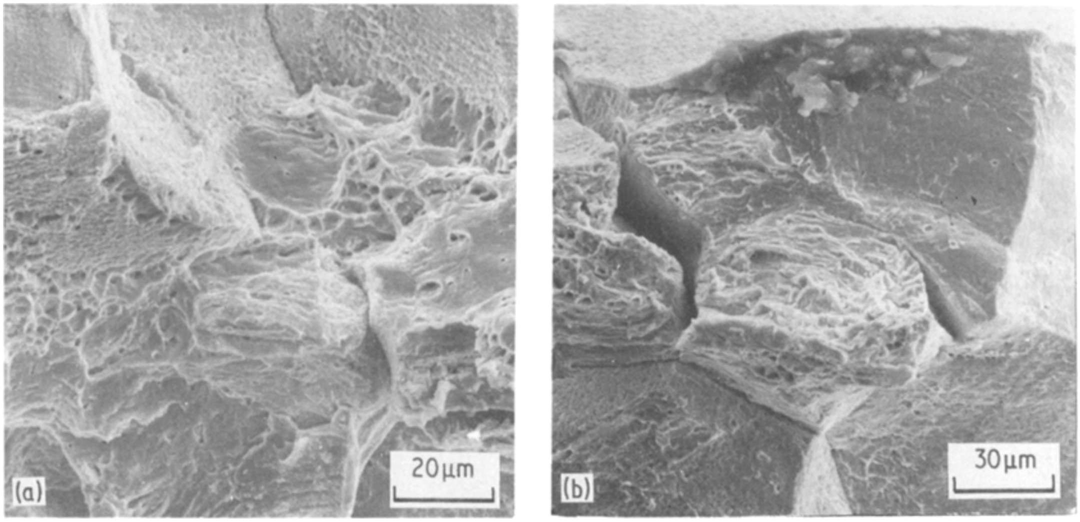

Figure 2 Scanning electron micrographs of fracture surfaces of sensitized steel specimens: (a) tested in air after 15 days of cathodic charging; (b) tested while undergoing cathodic charging.

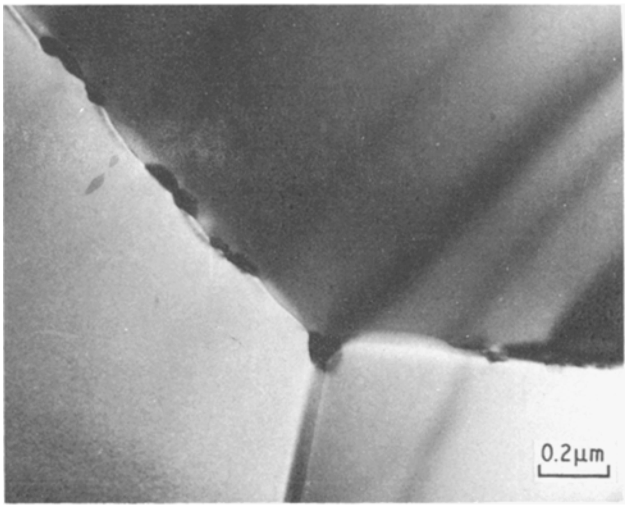

Figure 3 Transmission electron micrograph showing grain-boundary carbides in the sensitized steel.

ductile fracture mode of microvoid coalescence. This form of internal hydrogen embrittlement results from an interaction between dissolved hydrogen and the microstructure to alter the ductile fracture process. Previous studies of hydrogen-assisted ductile fracture in austenitic alloys have been performed on specimens which have been charged with hydrogen by either high-temperature or high-pressure techniques [15, 18]. Dimple size reduction due to hydrogen, represent large increases in dimple density and therefore in microvoid nucleation rates. The complex relations between dimple size changes and hydrogen induced ductility loss are described by Thompson [19]. The decreased dimple size observed [9] in hydrogen charged 304L and 309S stainless steel specimens shows that hydrogen affects fracture processes by accumulating at the inclusion sites and reducing the interface strength. Absorbed hydrogen could have two effects on the fracture process: it can lead to brittle cleavage-like fracture and it can also influence the ductile fracture process, as previously described. It seems likely that the role of hydrogen would be different in the two cases and thus it is possible that cleavage-like fracture require α-martensite, while the ductile case does not [8]. Hannien *et al.* [20] charged annealed thin specimens with hydrogen through cathodic polarization and subsequent tensile testing. They show that a 316L steel can be severely embrittled by hydrogen and that the embrittlement process produces an extremely brittle cleavage-type fracture without any evidence of ductile fracture. These results are in contrast to our present observations which, for the annealed material, show only microvoid coalescence which produces ductile rupture.

The ferrite measurements on the faces of the specimens did not show any evidence of α-martensite. Transmission electron microscopy (TEM) shows clearly that no α-martensite was formed in connection with the hydrogen embrittlement process. TEM studies of the fracture surfaces have revealed dislocation structures which suggest the existence of a metastable phase, probably ϵ-martensite, during the cathodic polarization. Sensitization seems both to facilitate the penetration of hydrogen along grain boundaries into the steel and to introduce susceptibility to fracture along grain boundaries (Fig. 2b). Fig. 3 shows a TEM micrograph of non-continuous grain-boundary carbides ($Cr_{23}C_6$) in the sensitized steel. The intergranular fracture observed in Fig. 2b is not due to the continuous grain-boundary carbides, as was reported by Fidelle *et al.* [11] for the sensitized 304 stainless steel. Our results are, however, in agreement with the results of Briant [6].

An unresolved question concerns the role of austenite transformation to α- and ϵ-martensite. This issue has become controversial and has been discussed extensively [1, 3, 7, 8, 21–23]. There is agreement that α-martensite increase the susceptibility of the material to hydrogen cracking. The role of ϵ-phase in the transfer of hydrogen from the environment is still unknown although there is some evidence in the literature that the presence of ϵ-martensite does not affect hydrogen cracking susceptibility [9]. Our study shows that no α-martensite formed in connection with the hydrogen charging process. It is suggested that α-

martensite formation is not a necessary condition for hydrogen cracking of the austenitic phase. This topic will be dealt with in future works.

It is believed that the issue of hydrogen-assisted cracking has become controversial due, in part, to the comparison of data from alloys which were not well characterized. For example, it cannot be assumed that a steel which is stable under one type of heat treatment or deformation or environment will be stable under different conditions.

4. Conclusions

This paper reports a study of hydrogen-assisted cracking in Type 316L stainless steel. The results show the following:

(a) Tensile tests show that, at room temperature, yield and ultimate strengths are not much affected by sensitization. Significant changes in the ductility were found due to the heat treatment and the method of charging. The sensitized 316L steel is much more susceptible to hydrogen cracking than the annealed steel.

(b) Examination of the fracture surfaces of specimens tested while cathodically charged shows considerable differences between the annealed and the sensitized specimens. The sensitized specimens were predominantly intergranular, while the annealed specimens show massive regions of microvoid coalescence producing ductile rupture.

(c) The fracture surfaces which showed hydrogen-induced ductility losses were completely ductile, with reduction in the dimple sizes.

(d) No evidence of α-martensite was found in connection with the hydrogen embrittlement process in the annealed or sensitized specimens. TEM studies of the fracture surfaces have revealed dislocation structures which suggest the existence of a metastable phase, probably ϵ-martensite, during the cathodic polarization.

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