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THE ROLE OF TWINNING AND TRANSFORMATION IN HYDROGEN EMBRITTLEMENT OF AUSTENITIC STAINLESS STEELS*

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THE ROLE OF TWINNING AND TRANSFORMATION IN HYDROGEN EMBRITTLEMENT OF AUSTENITIC STAINLESS STEELS

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Abstract

Internal hydrogen embrittlement may be viewed as an extreme form of environmental embrittlement that arises following prolonged exposure to a source of hydrogen. Smooth bar tensile specimens of three stainless steels saturated with deuterium (∿200 mol D_2/m^3) were pulled to failure in air at 200-400 K or in liquid nitrogen at 78 K. In Type 304L stainless steel and *Tenelon** ductility losses are a maximum around 200-273 K; Type 310 stainless steel is not embrittled at this hydrogen concentration. A distinct change in fracture mode accompanies hydrogen embrittlement, with fracture proceeding along coherent boundaries of pre-existing annealing twins. This fracture path is observed in *Tenelon* at 78 K even when hydrogen is absent. There is also a change in fracture appearance in specimens with no prior exposure to hydrogen if they are pulled to failure in high-pressure hydrogen. The fracture path is not identifiable, however. Magnetic response measurements and changes in the stress-strain curves show that hydrogen suppresses formation of strain-induced α'-martensite at 198 K in both Type 304L stainless steel and *Tenelon*, but there is little effect in Type 304L stainless at 273 K.

Introduction

Austenitic stainless steels are much more resistant to hydrogen embrittlement than are ferritic or martensitic stainless steels (Walter, 1968). At one time, austenitic steels were even thought to be immune to hydrogen degradation of mechanical properties, a point of view that has been dispelled by the extensive investigations of the past ten years (Louthan, 1972). Most types of stainless steel have been shown to lose ductility if a sufficiently high hydrogen concentration is reached during charging or if the external hydrogen pressure is great enough. For any given type of stainless steel, mechanical and thermal processing, as well as variations in composition, alter the extent of hydrogen embrittlement (Louthan, 1974; Odegard, 1976; McCoy, 1973; and Thompson, 1974).

* U. S. Steel trademark for 18Cr-15Mn-0.4N alloy.

Explanations for the differences in susceptibility to hydrogen embrittlement among the types of stainless steel have tended to emphasize (1) the presence of martensite prior to loading or (2) the strain-induced transformation to martensite during deformation (Vennett, 1967; Benson, 1968). This emphasis followed naturally from the pronounced susceptibility of ferritic and martensitic steels to embrittlement and the earlier correlation of susceptibility of austenites to embrittlement with their stability. Although the correlation of hydrogen embrittlement with martensitic phases is broadly true, loss of ductility is observed also in the stable austenites such as Type 310 stainless steel (Whiteman, 1965; Holzworth, 1969). The presence of martensite, therefore, is not a necessary condition for hydrogen embrittlement, in spite of continued support for this view. On the other hand, the presence of martensite may well be a sufficient condition, as all martensitic steels are embrittled by hydrogen.

Loss of tensile ductility is usually greater in materials saturated with hydrogen than in those same materials when tested in a hydrogen environment. Furthermore, fracture mode changes extend over a larger surface area and are more readily observed and analyzed. The nature and mechanism of damage are probably the same; therefore, results from tests of hydrogen-saturated specimens described here are relevant to an understanding of hydrogen-environment embrittlement.

Mechanical Behavior

The role of strain-induced transformation in hydrogen embrittlement of austenitic stainless steels was evaluated by analyzing tensile data from three types of steel representing different modes of response to deformation. Type 304L stainless steel transforms to both ε- and α'-martensite, *Tenelon* transforms to ε-martensite, and Type 310 stainless steel shows no transformation. Nominal compositions and structures are given in Table I.

Table I

Nominal Compositions and Structural Characteristics of Austenitic Stainless Steels

Alloy	Composition, wt %					Structure		
	Cr	Ni	Mn	C	N	Twins	α'	ε
304L	19	10	2	0.03	-	Yes	Yes	Yes
310	25	20	2	0.25	-	No	No	No
Tenelon	18	-	15	0.10	0.4	Yes	No	Yes

Ductility changes accompanying saturation (∿200 mol/m^3) with deuterium were slight in Type 310 alloy, very pronounced in Type 304L alloy at 198 and 273 K and significant at all test temperatures in *Tenelon*, as seen in Table II and Figure 1. Both uniform elongation and necking strain are reduced by hydrogen gas. The embrittlement was most pronounced in the temperature range 198 to 273 K in both *Tenelon* and Type 304L stainless steel (Hobson, 1953). Note that *Tenelon* fractures in a brittle mode at 78 K even without hydrogen addition.

Table II

Ductility Loss Following Exposure to High-Pressure Hydrogen

Test Temp, K	Ductility Loss, percent					
	304L		310		*Tenelon*	
	RA[a]	UE[b]	RA	UE	RA	UE
380	13	0	0	0	20[c]	0[c]
273	55	45	0	0	43	4
198	70	28	0	0	38	30
78	0	0	0	0	27	0

a. Reduction of area.
b. Uniform elongation.
c. Test at 350 K.

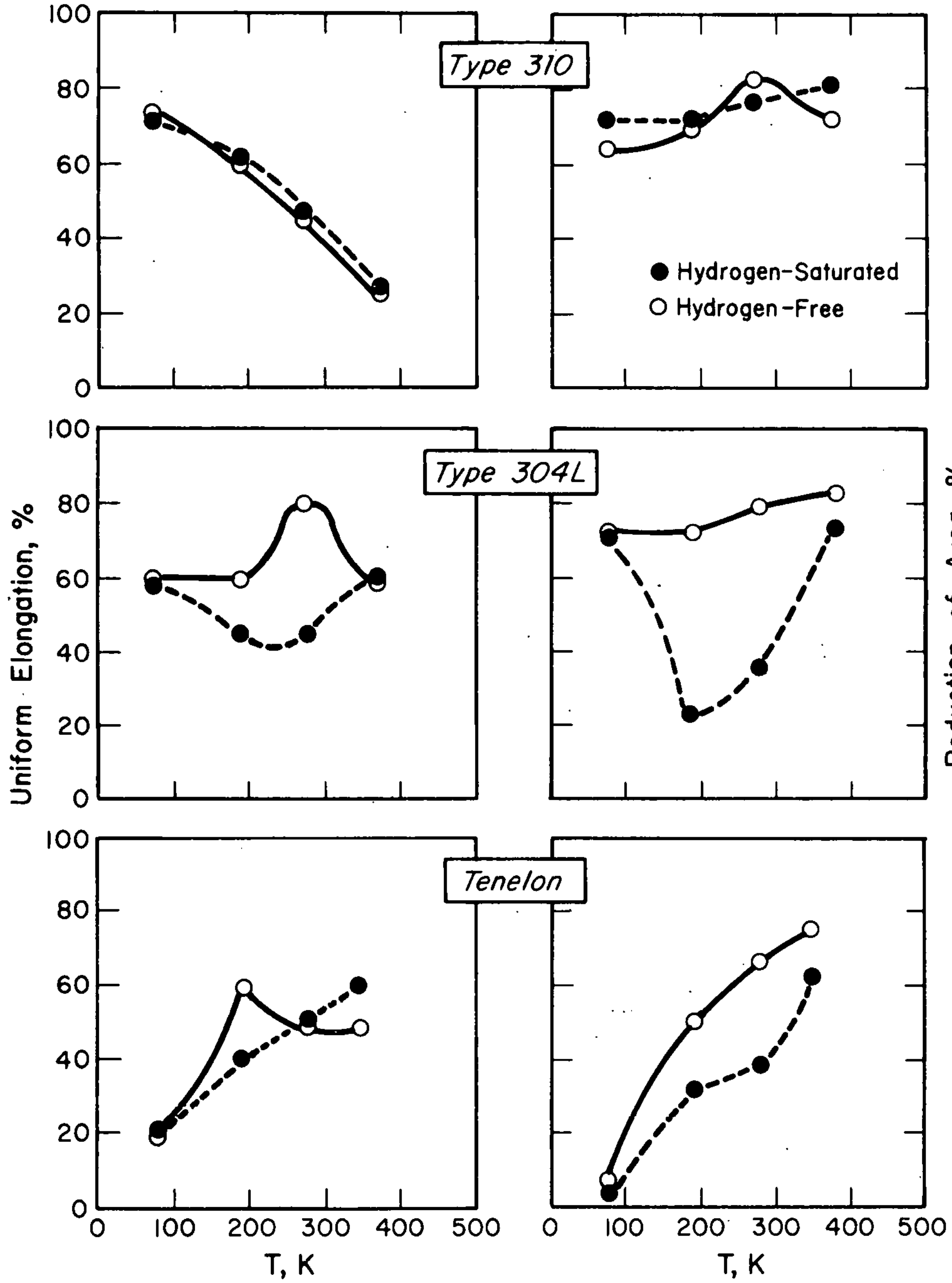


FIGURE 1. Temperature-Ductility Relationships for Three Austenitic Stainless Steels

Analysis of Stress-Strain Data

The strain-induced formation of α'-martensite can significantly change the deformation behavior and the onset of plastic instability during tensile deformation of metastable austenites (Bressanelli, 1966). These changes are readily apparent if the true stress-strain curve is analyzed in terms of the function η (Guimaraes, 1975), which represents the rate of change of the load-carrying capacity of the specimen with strain per unit cross-sectional area. The function is defined by

$$\eta = \frac{d\sigma}{d\varepsilon} - \sigma \qquad (1)$$

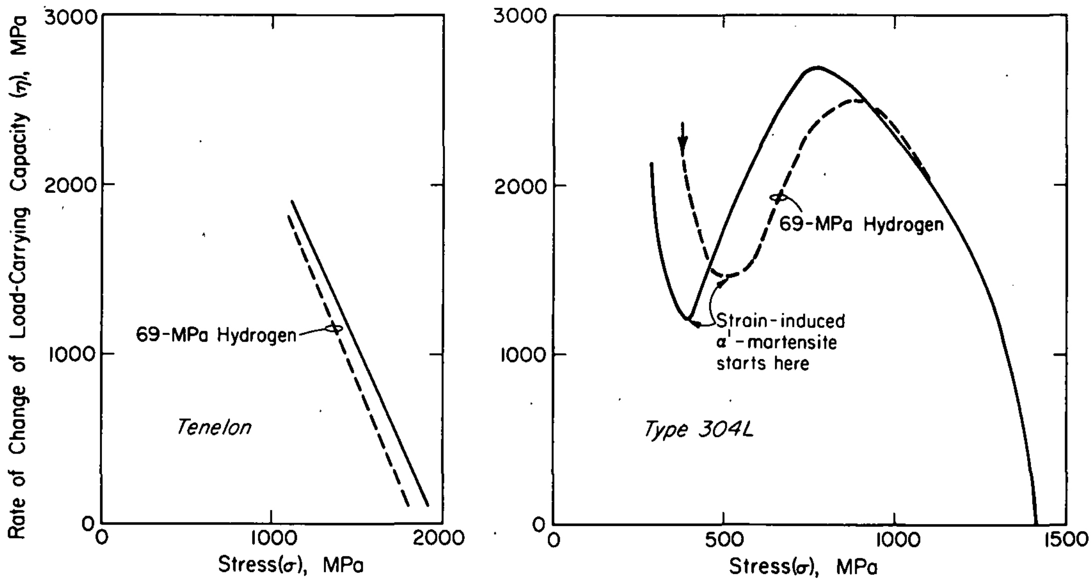
where $d\sigma/d\varepsilon$ is the instantaneous slope of the stress (σ)-strain (ε) curve and σ is the stress at the same point. Two types of behavior for η that are commonly observed in austenitic steels are: Type A, a linear decrease in η with increasing σ, and Type B, a roughly S-shaped curve, which is caused by the large strengthening of the strain-induced α'-martensite. Both types of behavior are shown in Figure 2.

Behavior of the three alloys that were tested corresponded to that of Type A (Figure 2a), with one exception: below M_d, the temperature required for formation of strain-induced α'-martensite, Type 304L stainless steel showed Type B behavior (Figure 2b). Transformation to ε-martensite, which occurs in *Tenelon* and during the early stages of deformation of Type 304L stainless steel, and to α'-martensite formation in *Tenelon* at 198 K do not modify the normal Type A behavior. Saturation of the alloys with hydrogen modified the behavior of Type 304L stainless steel by suppressing Type B behavior slightly, Figure 2b, but had no effect on *Tenelon* or Type 310 stainless steel other than to shift the curves slightly because of the strengthening effect of hydrogen in solution.

Modification of Type B behavior by hydrogen in Type 304L stainless steel implies that hydrogen either suppresses the strain-induced transformation of austenite to α'-martensite or lowers the capability of the α'-martensite to harden the alloy. Published studies on the effect of hydrogen on the $\gamma \rightarrow \alpha'$ transformation indicate that the martensite start temperature (M_s) in several metastable austenitic steels is unchanged (Burke, 1976) and that low concentrations ($\sim$30 mol/m^3) of hydrogen do not alter the strain-induced α'-martensite formation at room temperature (Thompson, 1976).

Magnetic Measurements

Additional evidence for changes in strain-induced formation of α'-martensite in hydrogen-saturated alloys was obtained by making magnetic response measurements on specimens of Type 304L stainless steel saturated with deuterium. Specimens were plastically deformed in small increments at 198, 248, and 298 K. Magnetic response and specimen diameter were measured after each strain increment. The results, Figure 3, show that



a. Type A Behavior b. Type B Behavior

FIGURE 2. Hydrogen Effects on Strain-Hardening of Two Stainless Steels at 198 K

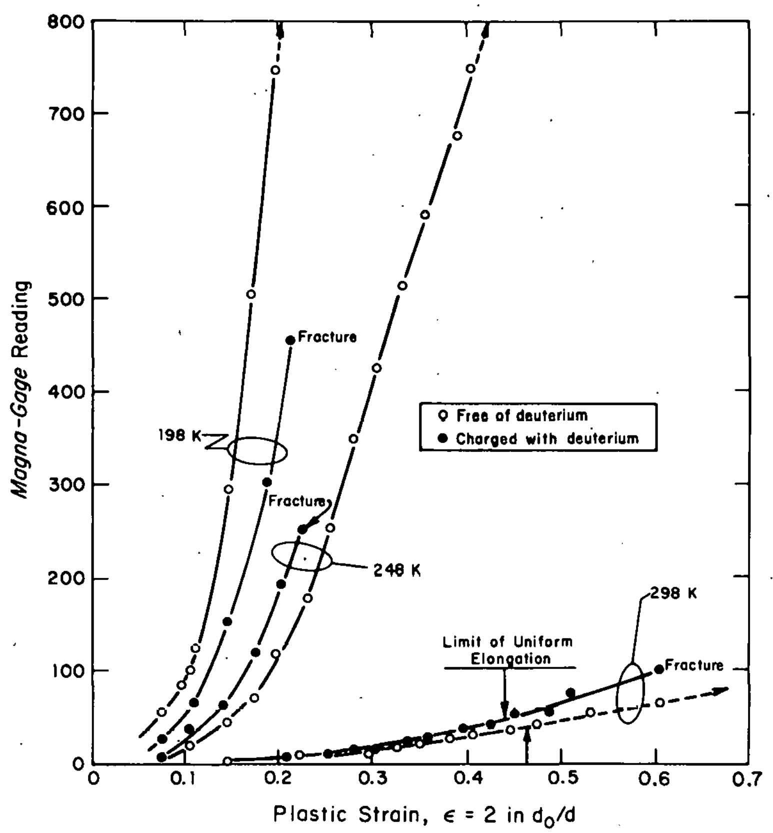


FIGURE 3. Effect of Hydrogen on Strain-Induced Martensite Formation in Type 304L Stainless Steel

at the two higher temperatures, hydrogen-free and hydrogen-saturated specimens do not differ significantly. The presence of hydrogen appears to have reduced the magnetic response by one-half in the pair of specimens deformed at 198 K.

A small amount of strain-induced α'-martensite forms in *Tenelon* deformed at 198 K, giving a *Magne-Gage** reading of 76 (Schaller, 1959), but not at the other test temperatures. This reading compares with a reading of ∿700 on Type 304L stainless steel at the same temperature and strain. This transformation was not observed in the deuterium-saturated specimen. As with Type 304L stainless steel, addition of sufficient hydrogen suppresses the formation of α'-martensite as determined by magnetic measurements.

In addition to suppressing strain-induced formation of α'-martensite, hydrogen retards the rate of isothermal phase transformation. Annealed specimens of Type 304L stainless steel were exposed to D-T gas at 69 MPa at 473 K for 15 days and then stored in liquid nitrogen along with companion specimens that were free of hydrogen. The extent of transformation to α'-martensite was determined in both sets of specimens with a vibrating sample magnetometer. The volume fraction martensite in the hydrogen-free specimens was 0.8 percent after an 86-day storage, whereas less than 0.1 volume percent martensite was formed in the D-T charged specimens after 430 days.

Fractography

Three varieties of austenitic steel in this study behaved in characteristically different manners after saturation with hydrogen (200 mol/m^3). Type 310 stainless steel was essentially unaffected by hydrogen at any of the test temperatures. Type 304L stainless steel was embrittled at the intermediate temperatures, and there was also a change in fracture mode. Behavior of *Tenelon* was similar to that of Type 304L stainless steel except that fracture of *Tenelon* at 78 K was brittle and of mixed mode even in the specimen that was free of hydrogen.

Scanning electron microscopy revealed distinctive features on the fractures: dimples, facets, striations, and secondary cracks. Alloy composition, test temperature, and the presence or absence of hydrogen controlled the fracture process and, therefore, the features that were present in each case. Ductile failure by microvoid coalescence is the common fracture mode for austenitic stainless steels that are free of hydrogen. Consequently, dimpled fracture surfaces were found in all hydrogen-free specimens except one, as shown in Table III. A mixed fracture with both facets and dimples occurred in hydrogen-free *Tenelon* tested in liquid nitrogen (78 K) to indicate that facet formation does not require the presence of hydrogen.

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* Trademark of American Instrument Company.

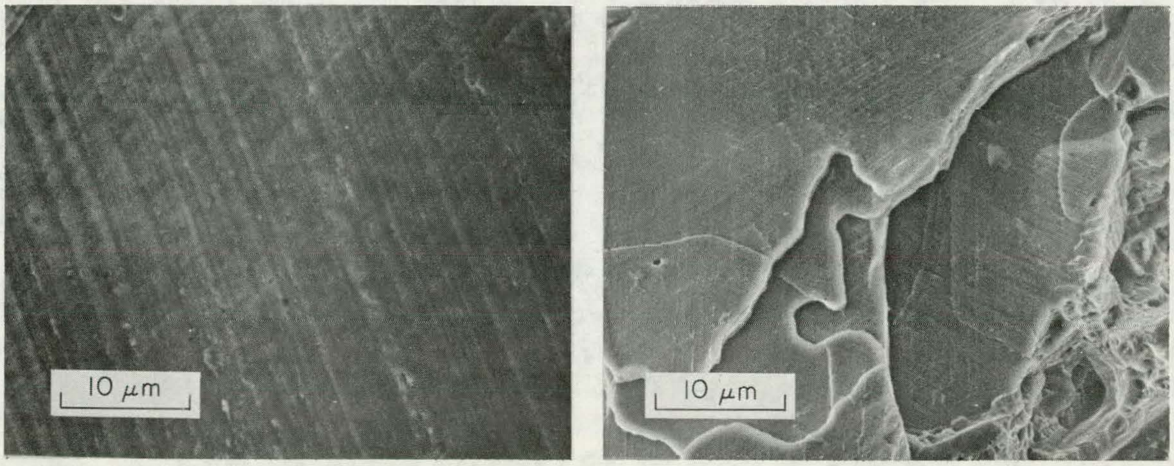
Table III

Fracture Modes Observed
on Austenitic Stainless Steels

Test Temp, K	304L		310		*Tenelon*	
	No D_2	D_2	No D_2	D_2	No D_2	D_2
380	D[a]	D	D	D	D	D
273	D	D, F[b], S[c]	D	D	D	D, F
198	D	D, F, S	D	D	D	D, F
78	D	D	D	D	D, F	D, F

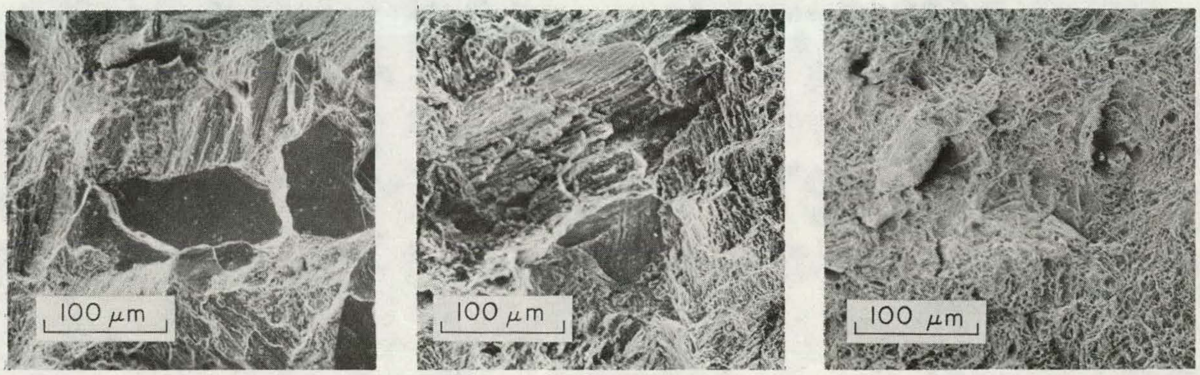
a. Dimple
b. Facet
c. Striation

Hydrogen embrittlement of Type 304L stainless steel and *Tenelon* was accompanied by a distinct change in fracture mode at test temperatures of 273 and 198 K. The wholly ductile rupture by dimple formation was replaced by a partly faceted fracture. In addition to the facets, embrittled specimens of Type 304L stainless steel contained striated areas and secondary cracks. In both steels, characteristics of the facets suggest that facets are formed along coherent boundaries of pre-existing annealing twins. Both alloys are heavily twinned in the annealed condition prior to hydrogen charging. The smaller facet size in the *Tenelon* corresponds to a smaller grain size and twin size. Examination of the facets shows that there are differences between the markings and traces on facet faces of *Tenelon* and Type 304L stainless steel, Figure 4. As the traces are believed to arise from slip bands or strain-induced transformation bands, the difference between *Tenelon* and Type 304L stainless steel reflects differences in details of the deformation characteristics of the two steels. The frequency of occurrence of the facets and the perfection of their formation depended on the deformation temperatures. Facets formed at 198 and 273 K were distinct and well formed, whereas facets formed in specimens tested at room temperature were poorly developed and less prevalent (Figure 5).



Type 304L *Tenelon*

FIGURE 4. Details of Markings on Facets of Hydrogen-Embrittled Stainless Steels



198 K 273 K 298 K

FIGURE 5. Variation in Facet Appearance with Test Temperature in Type 304L Stainless Steel

Embrittlement Mechanisms

Austenitic stainless steels may be divided into two categories on the basis of the relative ductility loss and fracture mode of a hydrogen-saturated specimen. The first category includes alloys such as Type 310 stainless steel where the ductility loss is relatively small and there is no change in fracture mode. Rupture is ductile and takes place by microvoid coalescence (MVC), with either an increase or a decrease in dimple size. A theory for the effect of hydrogen on MVC has been developed recently which accounts for the main features of this category of hydrogen embrittlement (Tien, 1976).

The second category includes those alloys where ductility loss may be relatively large and a change in fracture mode occurs. Type 304L stainless steel is the prototype of this category. Generally the fracture is mixed mode, consisting of planar facets within a connecting MVC network. Available information indicates that there is a transition from category one to category two at a stacking-fault energy (SFE) of about 40 mJ/m^2.

A mechanism for formation of the facets has not been developed, but must take several observations into account. Facet formation does not require the presence of either strain-induced α'-martensite or hydrogen. Frequency of occurrence of facets is increased and perfection of formation of the facets is improved by lowering the deformation temperature and adding hydrogen to the alloys. Other factors which are an integral part of the behavior of austenitic stainless steels are: a decreasing SFE with decreasing temperature and resulting preference for ε-martensite formation over deformation twinning with decreasing temperature (Lecroisey, 1972); an increase in the ratio of extrinsic to intrinsic stacking fault probably upon addition of hydrogen (Burke, 1976); and the general observation that the coherent boundaries of annealing twins are barriers to dislocation motion. The appearance of the facets and these observations and factors suggest a dislocation mechanism for fracture along coherent boundaries of pre-existing annealing twins (Caskey, 1977). If the suggested mechanism is substantiated, faceted fracture should only occur in austenitic steels that contain annealing twins and should be absent in other alloys where annealing twins are infrequent. The transition from ductile to brittle fracture correlates with decreasing SFE as the frequency of annealing twins increased. In addition, the efficiency of hydrogen transport by dislocations increases with decreasing SFE (Tien, 1976), and accumulation of hydrogen at localized sites (the twin boundaries) attains a higher concentration at relatively low macroscopic strains. The temperature range of maximum embrittlement will depend on a balance between binding energy of hydrogen to dislocations; the temperature dependence of SFE, which controls the quantity of hydrogen carried by the dislocations and the tendency for coplanar slip; and the strength of the alloy.

Hydrogen-environment embrittlement is believed to be of the same fundamental nature as internal embrittlement and to proceed by the same mechanisms. Surface conditions and gas-phase compositions will influence environmental embrittlement because the hydrogen must cross the gas-solid interface to cause embrittlement. The appearance of the fractures will also differ from most of those described here, because environmental tests are normally conducted at room temperature where facet formation is less distinct and less frequent than at lower temperatures. Specimens of Type 304L stainless steel and *Tenelon* tested in 69-MPa hydrogen at room temperature did not show clearly defined facets; however, areas of poorly-defined brittle fracture suggestive of facets were seen, Figure 6.

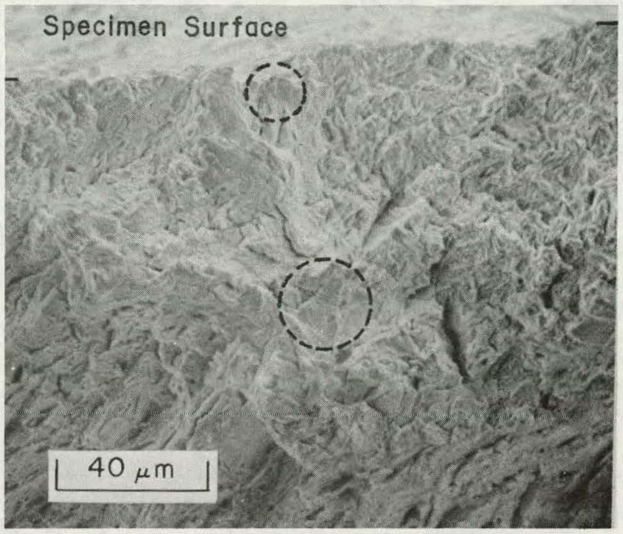


FIGURE 6. Poorly Developed Facets (at Circles) in Type 304L Stainless Steel Fractured in High-Pressure Hydrogen

Conclusions

Hydrogen embrittlement of Type 304L stainless steel and *Tenelon* is accompanied by a change in fracture mode. Cracks propagate along properly oriented coherent boundaries of pre-existing annealing twins developing facets on the fracture face.

Facet formation does not require strain-induced α'-martensite nor the presence of hydrogen. The mechanism is apparently inherent in austenites of low stacking-fault energy.

Hydrogen suppresses α'-martensite formation at 198 and 78 K in Type 304L stainless steel and at 198 K in *Tenelon*.

The formation of strain-induced α'-martensite is not necessary for hydrogen embrittlement of austenitic stainless steels.

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