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FRACTOGRAPHY OF HYDROGEN-EMBRITTLED IRON-CHROMIUM-NICKEL ALLOYS

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ABSTRACT

Tensile specimens of iron-chromium-nickel base alloys were broken in either a hydrogen environment or in air following thermal charging with hydrogen. Fracture surfaces were examined by scanning electron microscopy. Fracture morphology of hydrogen-embrittled specimens was characterized by: changed dimple size, twin-boundary parting, transgranular cleavage, and intergranular separation. The nature and extent of the fracture mode changes induced by hydrogen varied systematically with alloy composition and test temperature. Initial microstructure developed during deformation processing and heat treating had a secondary influence on fracture mode.

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INTRODUCTION

Hydrogen embrittlement of iron-chromium-nickel base alloys indicates a reduced ductility or fracture toughness because of the pressure of hydrogen. Tensile strength, however, is not necessarily decreased. There is no unique fracture mode associated with hydrogen-assisted fracture of these alloys, but more than one fracture mode has been reported, such as intergranular separation,[1] faceted fracture,[2] quasi-cleavage,[1] striations,[3] dimpled failure,[3] and twin-boundary parting.[4] However, some alloys exhibit a singular mode of hydrogen-assisted fracture.

Investigations of hydrogen-assisted fracture at the Savannah River Laboratory have covered a large number of alloys in the iron-chromium-nickel system. Hydrogen effects on fractography and mechanical properties of some alloys have been reported.[5] In this report, fracture modes studied by scanning electron microscopy (SEM) are correlated with alloy composition and test conditions. Secondary effects of thermal and mechanical processing on fracture morphology are also described.

HYDROGEN-ASSISTED FRACTURE

There are several generally recognized processes for hydrogen embrittlement of metals and alloys. These processes include hydride formation, hydrogen-reaction embrittlement, and hydrogen-assisted fracture (HAF). However, only HAF is found in iron-chromium-nickel alloys. In HAF, changes in strength, fracture toughness, crack growth rate, or ductility occur with no visible hydride formation or demonstrable chemical reaction that yields a gaseous reaction product.

Hydrogen effects on the mechanical properties of commercial iron-chromium-nickel alloys have been studied because of the wide interest in finding high-strength alloys resistant to both corrosion and hydrogen damage for applications in the petrochemical and chemical processing industries, space vehicles, and hydrogen production and storage. Hydrogen environment embrittlement (HEE) of these alloys can be evaluated by tensile ductility or crack growth rate of suitably loaded specimens in the presence of gaseous hydrogen at room temperature. As seen from data in Figure 1, susceptibility of the specimens to HEE varies widely as measured by loss of tensile ductility. The data have been plotted as if all alloys were simple ternary alloys although several contain additions of niobium, molybdenum, titanium, aluminum, or copper. These alloying elements are often added to 1) prevent sensitization, 2) toughen the alloys, or 3) render them precipitation hardenable. A similar pattern of response to hydrogen has been obtained in tensile tests of specimens exposed to high-pressure hydrogen gas for prolonged times to dissolve hydrogen into the alloys[5] and in cathodically charged alloys[6].

Severity of hydrogen damage in stainless steels is temperature dependent. Typically, the temperature for maximum hydrogen damage is around 200 to 250 K, as measured by tensile ductility of gas phase charged specimens. The magnitude of ductility loss at the ductility minimum varies with alloy composition.

FRACTOGRAPHY

Specimens of several alloys (Table I) were broken in tension either in high-pressure (69 MPa) hydrogen gas or in air at atmospheric pressure after prolonged (3-week) exposure to high-pressure hydrogen gas at 620 K. Fracture surfaces were inspected on an AMR Model 900 scanning electron microscope.

Four characteristic fracture morphologies were observed during the examination for the hydrogen-assisted fracture of the alloys (Figure 1): dimpled fracture, twin-boundary parting, transgranular cleavage, and intergranular separation. These fracture morphologies are illustrated in Figures 2 through 5. Each variety of fracture tended to be most prevalent over a limited region of composition as delineated in Figure 6. However, fractures were usually mixed with two or more morphologies present, although hydrogen-assisted fracture of nickel was nearly 100% intergranular separation. Boundaries between the several regions were not sharply defined, but there is a gradual shift from one fracture mode to another.

Dimpled fracture is the usual mode of failure for ductile alloys, such as the stainless steels (Figure 2). All fractures of iron-chromium-nickel alloys were, to some extent, ductile with areas of dimpled fracture evident even when gross ductility was only 10 to 20%. With some alloys and test conditions, a change in dimple size was evident for the HAF. Dimple diameters were measured for several Type 304L stainless steel specimens, both with and without prior exposure to hydrogen. The average dimple size in HAF was always smaller than that for fracture of hydrogen-free specimens. A correlation between loss of tensile ductility and change in dimple size was reported for austenitic steels.[7] The larger the change in dimple size, the greater the ductility loss. However, the present results from tensile tests at 250 and 270 K do not fall on the published curve, which was derived from room temperature tensile tests.

Twin-boundary parting, shown in Figure 3, was the common mode of HAF in Type 304L stainless steel.[5] Twin-boundary parting has also been observed in iron-chromium-manganese base alloys.[5] The incidence of this fracture mode was strongly dependent on temperature and composition. For example, twin-boundary parting was observed in Type 304L stainless steel but not in Type 316 stainless steel. The most clearly defined example of twin-boundary parting occurred at test temperatures of 200 to 250 K in Type 304L stainless steel.

Examination of numerous fractures has shown that twin-boundary parting is characterized by the following features:

- A single facet extends over one grain only.
- Facets often have steps.
- Traces of deformation bands in the underlying grain are visible.
- Opposing halves of the fracture match.
- Facets are slightly curved because of lattice bending prior to separation along the twin boundary.
- River patterns are never seen.

Transgranular cleavage was a form of HAF observed in ferritic and martensitic stainless steels. For example, the fracture mode of 17-4PH was predominantly transgranular cleavage as seen in Figure 4. This fracture mode can yield facets similar to those of twin-boundary parting, but the facets are readily distinguished at high magnification by the occurrence of river patterns and the absence of deformation traces.

Intergranular separation was characteristic of HAF of alloys containing more than about 30 or 35% nickel but was not limited to these alloys. Commercial grades of nickel displayed the most clearly delineated intergranular separation (Figure 5). However, specific thermal treatment could evoke intergranular separation in most alloys. In the case of nickel, intergranular separation was increased by prolonged testing at 770 K.

Specimens of Type 304L stainless steel were sensitized by heating to 620 K. This treatment precipitates carbides at the grain boundaries. HAF of these specimens was predominantly intergranular separation, which was similar to that seen in Inconel™ 718 (Huntington Alloys, Inc.) (Figure 5).

CORRELATION OF FRACTURE MODE WITH COMPOSITION

Fracture modes for HAF of iron-chromium-nickel alloys vary with percent of nickel in the alloy. Alloys such as 17-4PH with only 4% nickel fail by transgranular cleavage. As the nickel content increases and the steels become austenitic, fracture by twin-boundary parting appears at around 10% nickel. A region of dimpled fracture occurs from 12 to 25 or 30% nickel, which is gradually supplanted by intergranular separation as the nickel content increases. However, there were only a few alloys in which only a single fracture mode was observed. In most instances, two or more fracture modes occurred, one of them being dimpled fracture.

Alloy composition is a controlling factor in HAF in two ways: 1) the base alloy determines slip character and phase stability during straining, and 2) impurity and trace elements may be strongly segregated and induce intergranular separation either alone or in combination with hydrogen. Planar slip is associated with low-nickel austenites and leads to high-stress concentrations at slip barriers, such as twin and grain boundaries. Sites of high-stress concentration may act as microcrack nucleation centers, especially in the presence of hydrogen, which may lower the cohesive strength. Austenite stability under strain is also correlated with nickel content. Formation of deformation twins, ε-phase, and α-martensite occurs more readily with lower nickel concentrations. Both slip planarity and phase stability are related to stacking fault energy. Greater resistance to hydrogen damage in austenitic steels has been correlated with higher stacking fault energy.[8] The transition from twin-boundary parting to dimpled fracture at around 12 to 14% nickel correlated with an increase in stacking fault energy to over 30 to 40 mJ/m^2.

Intergranular separation in all of the stainless steels may be attributable to impurity segregation. Sulfur in high-nickel alloys and phosphorous in austenitic steels are known to cause intergranular failures.[9] These impurities are not the only causes of intergranular fracture, however. Sensitization of austenitic steels leads to carbide precipitation and grain boundary regions depleted in chromium and causes intergranular fracture in Type 304L stainless steels but not Type 309S stainless steel.[10] These examples illustrate the sensitivity of HAF to relatively small changes in either base alloy composition or impurity content. Control of melting, casting, and mechanical and thermal processing becomes more important for hydrogen service than for service in air. Small changes in local composition due to variations in process control can develop conditions for HAF in an otherwise resistant alloy.

CONCLUSIONS

Hydrogen-assisted fracture of iron-chromium-nickel base alloys may occur through several fracture modes: dimpled fracture, twin-boundary parting, intergranular separation, or transgranular cleavage. None of these fracture modes is unique to hydrogen-assisted fracture. The presence of hydrogen, however, evokes brittle fracture modes under loading and temperature conditions where ductile failure by dimple formation ordinarily occurs. Base alloy composition is the primary determinant of fracture mode through properties, such as crystal structure, slip character, and phase stability. Minor alloying elements and impurities may influence fracture mode by segregating to internal boundaries.

REFERENCES

1. R. M. Vennett and G. S. Ansell. "The Effect of High-Pressure Hydrogen Upon the Tensile Properties and Fracture Behavior of 304L Stainless Steel." Trans. ASM 60, 242-251, (1967).
2. R. B. Benson, Jr., R. K. Dann, and L. W. Roberts, Jr. "Hydrogen Embrittlement of Stainless Steel." Trans. Metall. Soc. AIME 242, 2199-2205, (1968).
3. M. R. Louthan, Jr., G. R. Caskey, Jr., J. A. Donovan, and D. E. Rawl, Jr. "Hydrogen Embrittlement of Metals." Mater. Sci. Eng. 10, 357-368, (1972).
4. G. R. Caskey, Jr. "Hydrogen Induced Brittle Fracture of Type 304L Austenitic Stainless Steel." Fractography and Materials Science, American Society for Testing Materials, Philadelphia, PA (to be published).
5. G. R. Caskey, Jr. "The Role of Twinning and Transformation in Hydrogen Embrittlement of Austenitic Stainless Steels." Environmental Degradation of Engineering Materials. M. R. Louthan, Jr. and R. P. McNitt, Ed., pp 437-449, Virginia Polytechnic Institute, Blacksburg, VA (1977).
6. R. Lagneborg. "Hydrogen Embrittlement in Austenitic and Nickel-Base Alloys." J. Iron and Steel Inst. 207, 363-366, (1969).

7. A. W. Thompson. "The Mechanism of Hydrogen Participation in Ductile Fracture." Effect of Hydrogen on Behavior of Materials, Proceedings of an International Conference, Jackson Lake Lodge, Moran, Wyoming, September 7-11, 1975. A. W. Thompson and I. M. Bernstein, Ed., pp 476-479, Metallurgical Society of AIME New York, NY (1976).

8. B. C. Odegard, J. A. Brooks, and A. J. West. "The Effect of Nitrogen on the Mechanical Behavior of Nitrogen Strengthened Stainless Steel." Effect of Hydrogen on Behavior of Materials, Proceedings of an International Conference, Jackson Lake Lodge, Moran, Wyoming, September 7-11, 1975. A. W. Thompson and I. M. Bernstein, Ed., pp 116-125, Metallurgical Society of AIME, New York, NY (1976).

9. W. Losch and I. Andreoni. "Grain Boundary Surface Phases Observed in Temper Embrittled High-Alloy Steels." Scripta Metall. 12, 277-281 (1978).

10. G. R. Caskey, Jr. "Hydrogen Assisted Fracture of Sensitized Type 304L Austenitic Stainless Steel." 109th Annual AIME Meeting, Las Vegas, Nevada, February 24-28, 1980 (to be published).

TABLE I

Nominal Alloy Composition, wt %

Alloy	Cr	Ni	Fe	Other
304L	19	10	68	-
309S	23	13	61	-
310	25	20	51.5	-
316	17	12	66	2 Mo
330	18	35	44	-
800H	21	33	-	-
718	19	54	18.5	3 Mo, 5 Nb, 1 Ti, 0.5 Al
17-4	17	4	72	4 Cu, 0.3 Nb + Ta
Ni	-	98	-	-
A286	15	26	54	1 Mo, 2 Ti, 2 Al

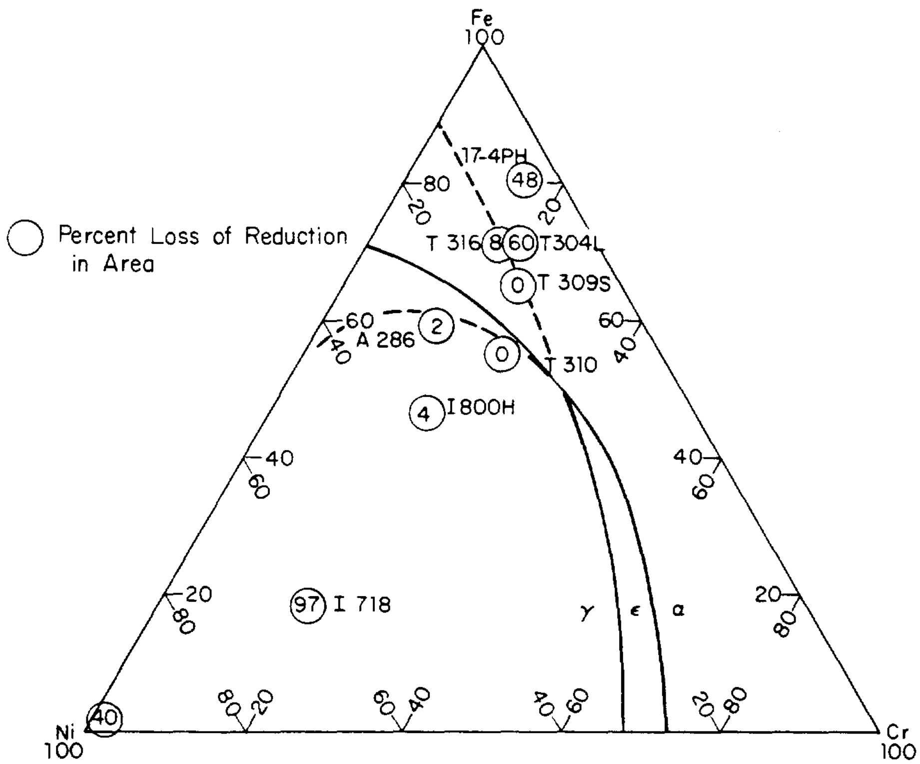
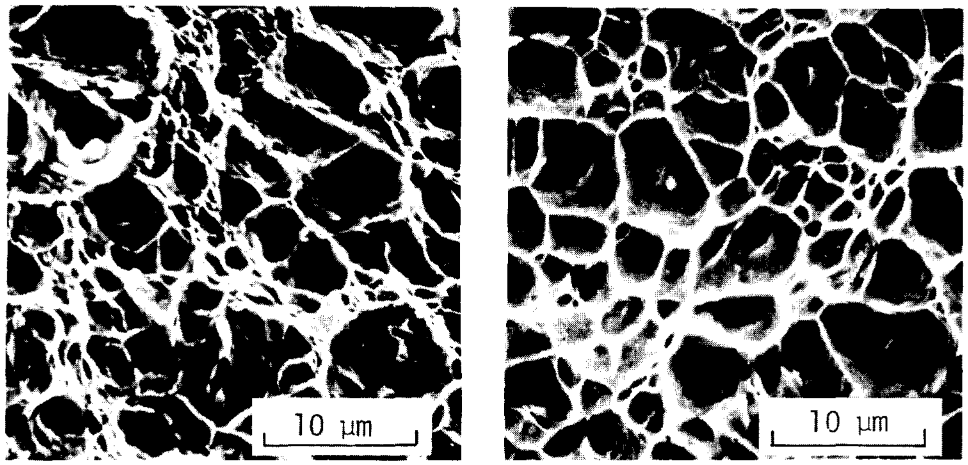


FIGURE 1. Hydrogen Environment Embrittlement of Iron-Chromium-Nickel Alloys.



No Hydrogen Hydrogen

FIGURE 2. Dimpled Fracture of Type 304L Stainless Steel.

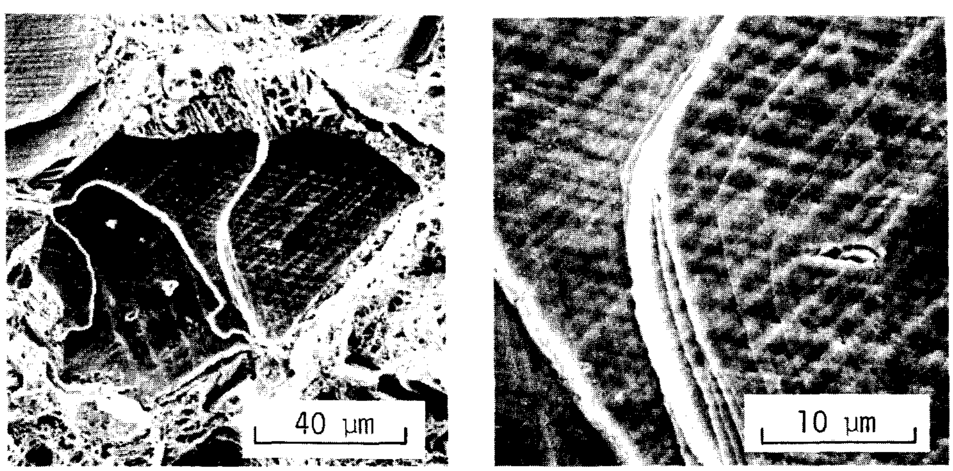


FIGURE 3. Twin-Boundary Parting in Type 304L Stainless Steel. High-Energy Rate Forged. Test at 200 K.

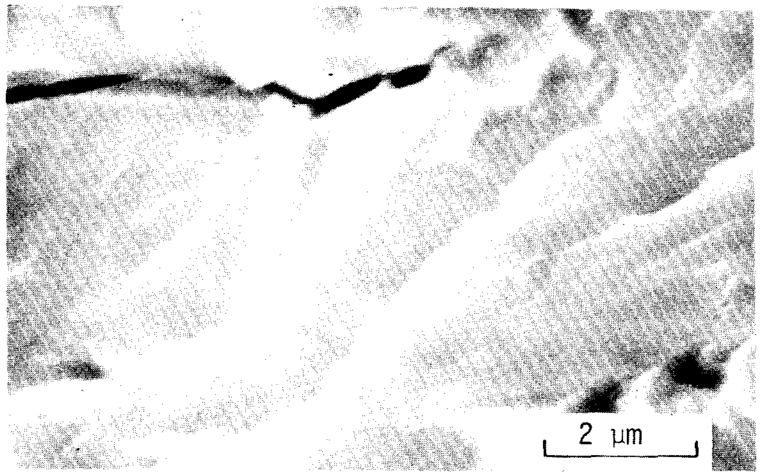
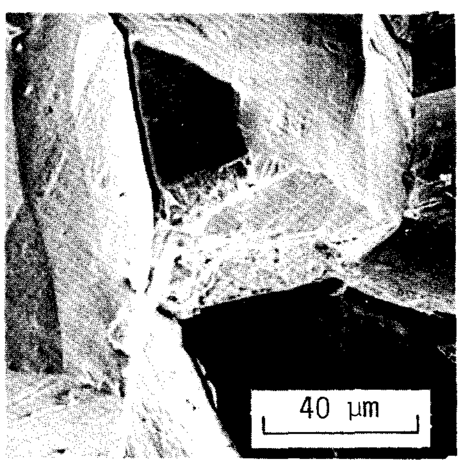
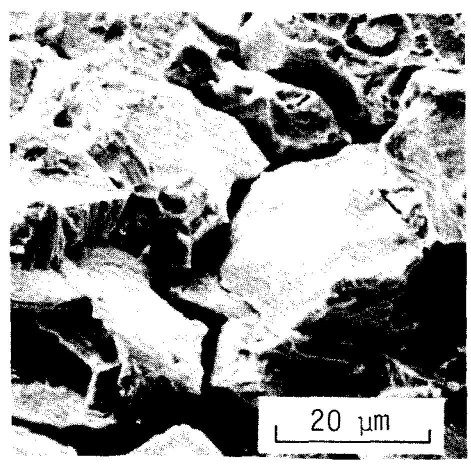


FIGURE 4. Transgranular Cleavage. 17-4PH Precipitation Hardenable Stainless Steel.



Nickel



Inconel™ 718

FIGURE 5. Intergranular Separation. Nickel and Inconel™ 718.

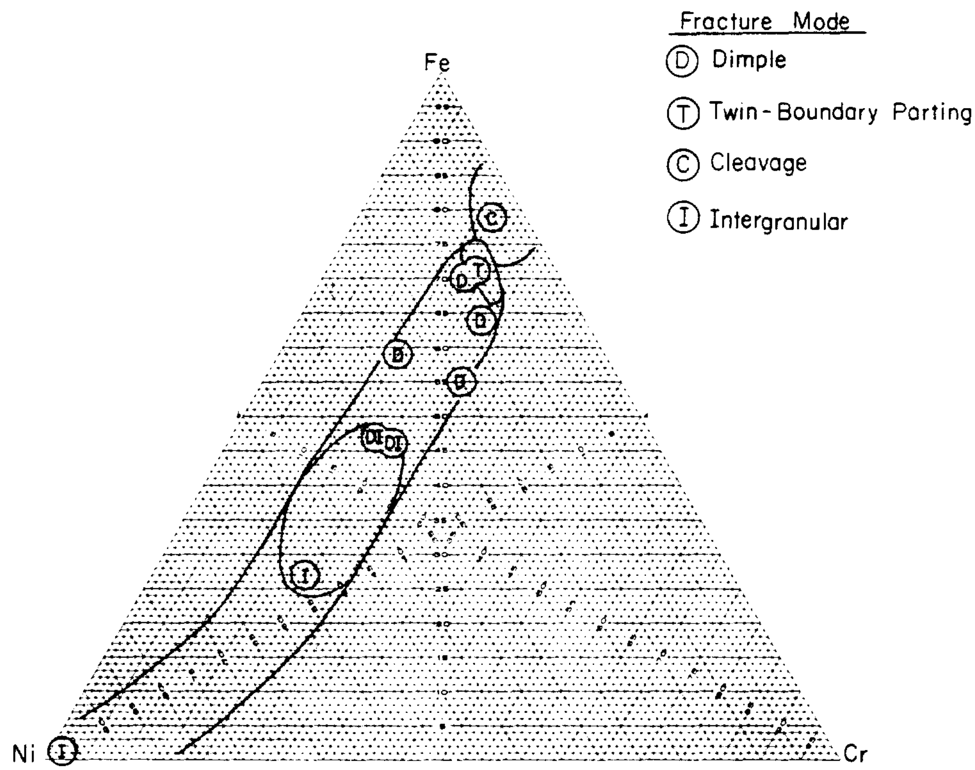


FIGURE 6. Composition Regimes for Fracture Modes Observed in HAF of Iron-Chromium-Nickel Alloys.