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HYDROGEN EMBRITTLEMENT OF THERMOMECHANICALLY TREATED 18Ni MARAGING STEEL

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Abstract

The influence of thermomechanical treatments on susceptibility to cracking in 100% relative humidity air and low pressure (93.3 KPa) gaseous hydrogen has been investigated for 18Ni(350 ksi) Maraging steel. Two thermomechanical treatments were studied, ausforming and marforming and compared with the standard solution treated and aged material. Although little difference exists for the strength and toughness values between these treatments, a two to five-fold increase in the stress intensity threshold for cracking was found for both the ausformed and marformed material. A dramatic difference in cracking kinetics was also apparent as shown by the failure times at comparable stress intensities.

Fractographic analysis showed that the primary fracture mode was 100% intergranular for the solution treated and aged samples while the ausform and marform failures were predominately quasi-cleavage or intergranular depending on orientation.

Finally, permeation and diffusion measurements were conducted on the above materials and these results are correlated with the environmental cracking behavior.

Introduction

Many previous investigations have considered the influence of various metallurgical variables on the susceptibility of ferrous alloys to stress corrosion cracking and/or hydrogen embrittlement. Bernstein and Thompson (1976) have recently reviewed much of this work and concluded that it should be possible to achieve notable improvements in a materials resistance to environmental degradation by suitable variations in heat treatment and/or thermomechanical processing. These techniques allow one to vary grain size and shape, dislocation density and distribution, slip mode and even crystallographic texture, all of which may be used to alter environmental cracking resistance.

Although maraging steels have long been known to possess superior resistance to hydrogen cracking when compared to quench and temper steels at equivalent strength levels (Phelps 1967), they are not immune to same. Indeed the threshold stress intensity for hydrogen cracking of 18Ni(350) Maraging steel is approximately 5.5-7.7 MPa $m^{\frac{1}{2}}$ while its fracture toughness in air is 38.5-44 MPa $m^{\frac{1}{2}}$ - a reduction of 80 pct. Certainly 18Ni(350) Maraging steel must be considered to be highly susceptible to hydrogen embrittlement.

Recently one of the present authors (Rack and Kalish 1974) has shown that selected thermomechanical treatments can enhance the high cycle fatigue resistance of 18Ni(350) Maraging steel. At the outset of this investigation, it was not clear if these same or similar treatments might enhance the stress corrosion/hydrogen cracking resistance of this steel, although other thermomechanical treatments have been shown to increase the stress corrosion-resistance of high strength aluminum alloys (Paton and Sommer 1973). The investigation reported herein was therefore undertaken to compare the relative susceptibility to hydrogen embrittlement of the normal solution treated and aged condition with the specially processed alloy.

Experimental Procedure

The chemical composition of the alloy used in this examination is shown in Table I. It is similar in composition to that used in a previous study (Rack and Kalish 1974) of thermomechanically treated 18Ni(350) Maraging steel. The room temperature mechanical properties and specific details of the conditions examined in this study are given in Table II. These results show that there is only a slight increase in strength and decrease in tensile ductility associated with the thermomechanically treated alloy. Furthermore, the fracture toughness does not appear to be affected by processing.

Table I: Chemical Composition of 18Ni(350) Maraging Steel

Composition (wt. pct.)

Ni	Co	Mo	Ti	Al	C	S	P
18.04	11.89	4.82	1.42	.14	.014	[illegible]	.010

Si	Mn	Cr	Cu	B	Zr
.05	.05	.05	.11	[illegible]	.01

Table 2: Mechanical Behavior of 18Ni(350) Maraging Steel

CONDITION*	0.2 PCT. YS (MPa)	UTS (MPa)	RED. AREA PCT.	K_{IC} (MPa $m^{1/2}$)
1088K-1h, AC (STD)	2281	2378	37	38.[illegible]
1088K-1h, AC + 70 pct. red. thickness 298K (MARFORM)	2447	2482	[illegible]5	3[illegible].[illegible]
1088K-1h, HQ + 70 pct. red. thickness 672K (AUSFORM)	2413	2468	27	37.6

*All conditions subsequently aged for 3h at 7[illegible]K, AC-air cool, HQ-hot quench

The stress corrosion/hydrogen susceptibility of these conditions were evaluated utilizing 2.5 mm thick compact tension samples (CT-1) machined from the original and thermomechanically processed plate, the crack orientation being either parallel or perpendicular to the rolling direction. Considerable care was taken during fatigue precracking to minimize the delay time effects previously observed when evaluating the threshold stress intensity for hydrogen cracking in ferrous alloys (Carter 1972). In all cases K_f, the final stress intensity during precracking was either one-half of $K_{threshold}$ or 7.7 MPa $m^{\frac{1}{2}}$ whichever was greater. All fatigue precracking was done at 298K in laboratory air.

Stainless steel chambers capable of being evacuated to less than 10^{-3} Pa and subsequently backfilled with high purity (99.999%) hydrogen were used in this study. Final gas pressure was held constant at 93.3 KPa, i.e., slightly greater than atmospheric pressure which is approximately 83.3 KPa at the altitude where the tests were conducted. Following evacuation and backfilling the precracked samples were loaded to various initial stress intensities and the resultant time to failure measured.

Stress corrosion cracking tests were also performed in 100% relative humidity air at 298K. These were conducted by enclosing the specimens in plastic bags containing sufficient H_2O to insure a saturated environment. Care was taken to avoid electrochemical effects by using insulated (ceramic coated) pins to eliminate any galvanic coupling between the test samples and fixtures. This system was also allowed to equilibrate for a minimum of 24 hrs. prior to initial application of the designed load. Specimens which had not failed after several thousand hours were removed from test, the crack was extended (marked) by additional fatiguing, subsequently failed and examined for environmentally assisted subcritical crack growth. The various fracture morphologies were subsequently characterized using standard metallographic and scanning electron microscopy techniques (Rack and Kalish 1974).

The hydrogen (deuterium) permeation and diffusivity was measured using the time-lag permeation method. Ultra-high vacuum techniques were employed and a residual gas analyzer was used to detect the permeating gas. Deuterium was used for all measurements because there was a large hydrogen background. A mercury diffusion pump was used to remove the permeating gas during the measurements. Mercury pumping gives a lower hydrogen isotope (H_2, HD, D_2) background than a conventional ion pump. The measurements were performed in the temperature range of 340K to 500K under deuterium pressures of 500 Pa to 40 KPa. The pressure dependence of the permeation followed Sieverts' law ($Q \sim P_{H_2}^{1/2}$) for all measurements. This pressure dependence implies that the permeation behavior was not dominated by surface contamination.

Measurements of the diffusivity were carried out by initially saturating the upstream sample face with hydrogen and waiting for steady state conditions to occur (permeation). The upstream gas was then removed and a new steady state attained (evolution). It was observed that the latter measurements generally gave slightly higher values for the diffusivity than did the permeation measurements.

Results

Time-to-failure measurements of pre-cracked samples in hydrogen or stress corrosion environments are really controlled and/or made up of the crack reinitiation time, the crack propagation rate and the fracture toughness. Table II shows that, in the present instance, processing differences do not materially affect the fracture toughness, therefore, these should not influence the time-to-failure measurements. Any differences in failure times observed in this investigation must therefore be due to changes in crack initiation and propagation behavior. Fig. 1 summarizes the results of the tests in 100% relative humidity air. They illustrate the dramatic effects of thermomechanical treatment on the threshold stress intensities for cracks propagating perpendicular to the principal processing direction.

Although the threshold stress intensity for cracking was not affected for a given crack propagation orientation when the environment was changed from 100% relative humidity to gaseous hydrogen the failure times were drastically decreased by this change, compare Figs. 1 and 2. In addition, the gaseous hydrogen results showed that the propensity for crack growth was highly anisotropic; the threshold stress intensity for both ausformed and marformed maraging steel were more than twice as high if the crack propagated in the transverse grain direction rather than in the longitudinal grain orientation. The same observations indicated that material history also had a drastic effect on time-to-failure at stress intensity levels above the threshold. To illustrate, when a crack was propagated parallel to the rolling direction, i.e., in the most susceptible orientation for the marformed and ausformed material, a five orders of magnitude difference in failure time between solution treated and aged and thermomechanically treated specimens was typically observed.

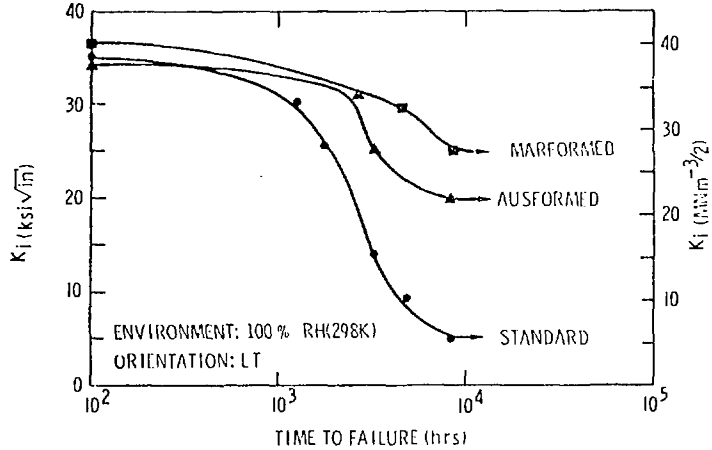

Fig. 1. Initial Stress Intensity versus time-to-failure in 100% RH Air. Crack Propagation perpendicular to rolling direction.

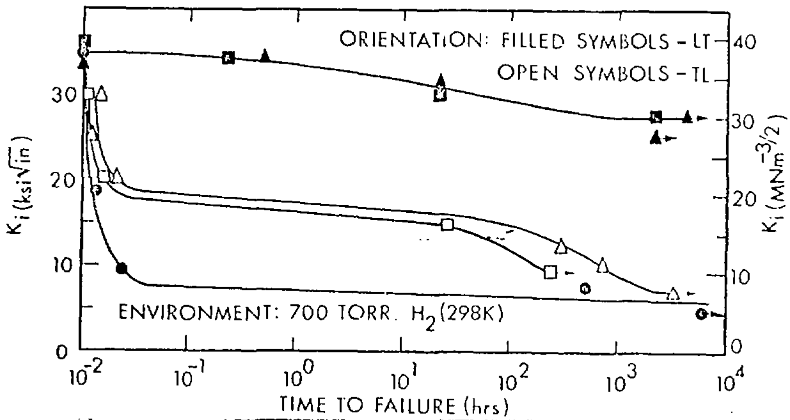

Fig. 2. Initial Stress Intensity versus time-to-failure in 9.33 KPa gaseous hydrogen; △, ▲ - Ausformed; □, ◘ Marformed; ● - solution treated and aged.

The fracture morphologies were quite varied and were strongly dependent upon processing history and orientation; however they did not appear to be environment specific. The general characteristics of the fracture surfaces are summarized below and depicted in Figures 3-5.

1. Solution Treated and Aged Specimens
   In all cases the fracture surfaces were 100% intergranular with profuse secondary cracking. Crack branching was also noted in the gaseous hydrogen tests. The latter is indicative at Stage II environmental crack velocities. In addition, no dimples were

observed on the intergranular surfaces.

2. Ausformed/Marformed Specimens
   a. LT orientation - cracks propagated perpendicular to the rolling direction. A predominately quasi-cleavage fract ce mode with limited secondary cracking and isolated regions of dimple rupture was observed.
   b. TL orientation - cracks propagated parallel to the rolling direction. The fracture surface was characterized by a "woody" or fiberous appearance which resulted from crack propagation through the heavily deformed structure. Large amounts of secondary cracking and quasi-cleavage fracture was also noted.

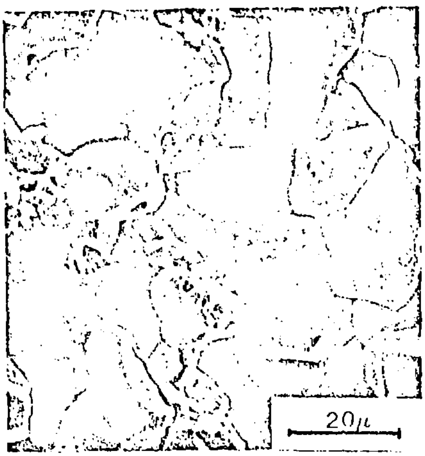

Fig. 3. Fracture surface of solution treated and aged material showing intergranular morphology and secondary cracking.

Failure times and threshold stress intensities correlated quite well with the above fracture morphologies, with the maximum failure time and threshold stress intensity being associated with the LT orientation of the ausformed/marformed material, these specimens exhibiting the tougher, more ductile fractures.

Table III shows a summary of the permeation and diffusion results for the standard solution treated and aged, and the ausformed and marformed treatments. The energies shown are activation energies calculated from an Arrhenius plot of the data with the room temperature values being established by suitable extrapolation of the data. Finally, the solubility values, S, are derived from the relationship between diffusivity, D, and permeability, Q: $S = Q/D$.

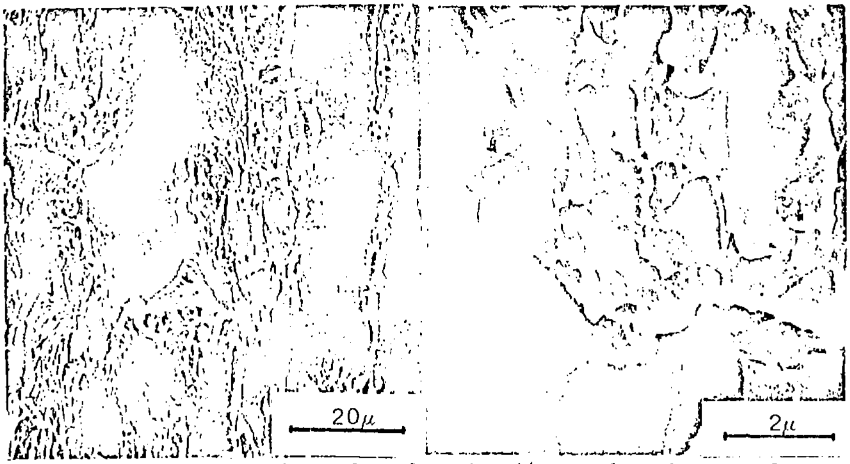

Fig. 4. Fracture surface of ausformed and/or marformed material for transverse crack propagation. Transgranular (quasi-cleavage) morphology with secondary cracking and isolated regions of dimple rupture were typical.

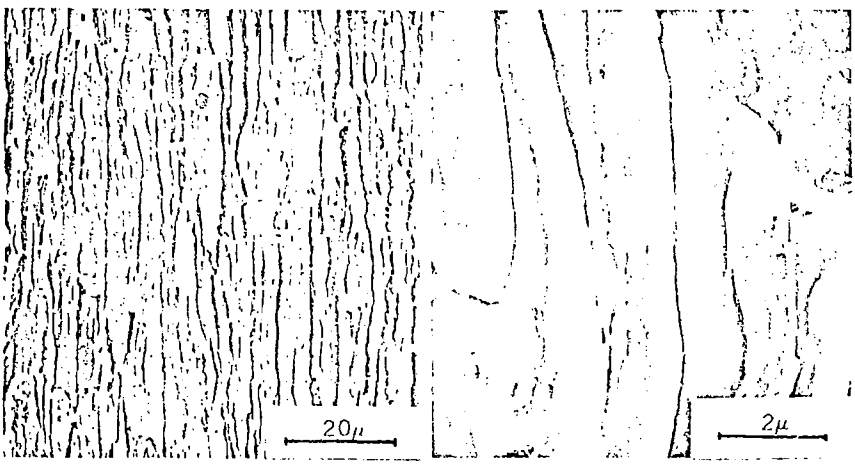

Fig. 5. Fracture surface of ausformed and/or marformed material for longitudinal crack propagation.

Table 3: Room Temperature Values for the Permeation, Diffusion, and Solubility of Deuterium in 18Ni (250) Maraging Steel

	Solution Treat. Plus Age	Ausform	Marform
<u>Diffusion</u>			
ΔE (kcal/g-atom)	11.2 ± 1.0	12.8 ± 1.0	12.4 ± 1.0
D_{RT} (cm^2/sec)	8.6×10^{-10}	2.2×10^{-10}	3.0×10^{-10}
<u>Permeation</u>			
ΔE (kcal/g-atom)	12.2 ± 1.0	13.3 ± 1.0	10.[illegible] ± 1.0
Φ_{RT} (cc(STP)/cm-sec-√atm)	2.3×10^{-11}	8.6×10^{-12}	5.7×10^{-11}
<u>Solubility</u>			
ΔH (kcal/g-atom)	1.0 ± 1.0	0.5 ± 1.0	-2.1 ± 1.0
S_{RT} (cc(STP)/cm^3 √atm)	0.027	0.039	0.14

Discussion

The thermomechanical treatments, as expected, result in an elongation or "pancaking" of the prior austenite grains and a significant anisotropic behavior in gaseous hydrogen. The higher threshold stress intensities for transverse crack propagation in the TMT material may be attributed, in part, to the change in cracking mode from intergranular to transgranular. It is clear that the maximum microstructural benefits realized by the TMT are associated with this forced transition in fracture path.

Although significant differences in the threshold stress intensities for transgranular or intergranular failures in ferrous alloys have not previously been reported, the marked improvements observed in the present examination correlate well with the microstructural changes previously reported for thermomechanical processing of maraging steel (Rack and Kalish 1974). Briefly, these changes are:

1. Coarser precipitate structure (small changes in interparticle spacing);
2. Increased dislocation density and finer cell structure-ausforming results in larger and more nearly equaixed cells than marforming;
3. Ausforming and marforming results in different textural descriptions.

The textural differences observed, as well as the other smaller differences between ausform and marform material seem to have little effect on susceptibility to hydrogen cracking. However, the precipitate and dislocation structure, which are expected to result in more homogeneous deformation and an increased number of trapping sites, e.g., that due to loss of particle-matrix coherency with increasing precipitate size, have been shown to result in improved hydrogen compatibility (Bernstein and Thompson 1976).

The longitudinal crack propagation tests did not show as significant an increase in the threshold stress intensity as the transverse tests. However, a large reduction in the crack growth rate, as shown by the increase in failure times, was observed for the former TMT material. Previous work (Parkins and Haney 1968, Rack 1975) has suggested that the more rapid intergranular cracking rates observed in normal solution treated and aged maraging steels may be associated with Ti rich particle formation on prior austenite grain boundaries. It appears that the introduction of a refined dislocation substructure within the near grain boundary region may mitigate the detrimental effect of these particles.

The permeation and diffusion measurements show a 2-4 fold increase in the diffusion coefficient for the TMT material although a simple correlation between these values and crack growth kinetics are questionable, particularly in view of the results of Williams and Nelson (1970) and Hudak and Wei (1973) for 4130 steel and maraging steel respectively. These authors have shown the crack growth rate kinetics to be about the same for these materials (3.8 Kcal/mole) although the diffusion coefficient for 4130 steel is 10^{-7} cm^2/sec (Kass 1975) at least 1-2 orders of magnitude higher than for the maraging steel. Crack growth rate studies are currently in progress at this laboratory and it is hoped that these will further define the kinetic parameters associated with the improved performance of TMT maraging steel in environments.

Summary

1. In 100% relative humidity air and 93.3 KPa gaseous hydrogen, the threshold stress intensities were found to be

$$K_{ISCC} = 5.5 \text{ MPa } m^{1/2}$$

for solution treated and aged material and

$$K_{ISCC} = 8.8 \text{ MPa } m^{1/2} \text{ (parallel to rolling direction)}$$

$$K_{ISCC} = 27.5 \text{ MPa } m^{1/2} \text{ (perpendicular to rolling direction)}$$

for either ausformed or marformed material.

2. Failure times in gaseous hydrogen increased by five orders of magnitude as a result of ausforming or marforming.
3. The susceptibility of the solution treated and aged material was notable with failures occurring in 93.3 KPa gaseous hydrogen being less than 60 seconds at stress intensities greater than 11 MPa $m^{1/2}$.
4. Fracture morphologies varied considerably and correlated well with associated failure times and threshold stress intensities, i.e., the more ductile features the fracture surfaces exhibited, the greater the time to failure and the higher the threshold stress intensity.

5. The improved resistance of the TMT material to hydrogen cracking (transgranular failures) appeared to be consistent with the expected changes in metallurgical variables (precipitate size, dislocation networks, etc.).
6. Finally there appeared to be little correlation between the stress corrosion/hydrogen susceptibility of 18Ni(350) Maraging steel and the bulk permeation/diffusion results - the latter do not vary significantly for the three conditions examined.

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