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HYDROGEN SOLUBILITY IN AUSTENITIC STAINLESS STEELS

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ABSTRACT

Hydrogen solubility was directly measured in specimens of Types 304L, 21-6-9, and modified A-286 austenitic stainless steels saturated with hydrogen at 69 MPa pressure at 470 K. Nitrogen in Type 21-6-9 stainless steel and precipitate morphology in the modified Type A-286 stainless steel altered the hydrogen solubility. Cold work and surface treatment had only minor effects on hydrogen solubility in the three stainless steels.

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INTRODUCTION

In this study, the effects of thermomechanical treatment and surface condition on hydrogen solubility in Types 304L, 21-6-9, and modified A-286 austenitic stainless steels were directly determined. Thin samples (0.13 cm) of the alloy (compositions given in Table 1) were charged to saturation in 10,000 psi (69 MPa) hydrogen gas at 470 K. The total hydrogen content of each sample was directly measured immediately after the charging treatment with the LECO™ RH-1 hydrogen gas determinator (Leco Corp., Saint Joseph, MI). Three thermomechanical treatments were studied: annealed, 100% cold-worked, and high-energy rate forged (HERFed). HERFed austenitic stainless steels are reported to be more compatible with hydrogen than annealed or cold-worked steels (1, 2). Hydrogen solubility was expected to be higher in HERFed specimens than in annealed specimens because of the higher dislocation density in HERFed material. Surfaces were electropolished or ground through 600 grit abrasive. Thermomechanical treatment did not change the hydrogen solubility in Types 304L or 21-6-9 stainless steels. However, the solubility of hydrogen in the modified Type A-286 was less in the HERFed specimens than in solution-annealed specimens. Apparently, the differing volume fractions of α' precipitate had a larger effect than the differing dislocation densities did on hydrogen solubility.

EFFECTS OF THERMOMECHANICAL TREATMENT

Hydrogen concentrations were expected to be higher in cold-worked and HERFed specimens because of the greater dislocation densities. The magnitude of this effect, however, can be shown to be small. To calculate the increased solubility due to increased dislocation density, the concentration of hydrogen dissolved in the lattice (C_L) and the concentration of hydrogen at dislocations (C_d) must be known. The total hydrogen concentration (C_T) is then determined from

$$C_T = C_L + C_d. \tag{1}$$

The lattice hydrogen may be determined from the annealed material. The hydrogen at dislocations may be calculated from (Reference 3)

$$C_d = fC_L e^{4,400/RT} \tag{2}$$

where 4400 cal/mole is the best estimate of the bonding energy for hydrogen to dislocations in austenitic steels, and f is the fraction of alloy atoms which are associated with a unit length of dislocation.

For severely cold-worked materials, the dislocation density was estimated at 10^{12} cm dislocation/cm^3 (Reference 4). The lattice parameter for austenitic stainless steels is approximately 3.55×10^{-8} cm. Therefore, f may be determined by calculating the number of alloy atoms associated with the length of dislocation line and the number of alloy atoms/cm^3 of alloy. For the dislocation density of 10^{12} cm dislocation/cm^3

$$f = \frac{10^{12}\ \frac{\text{cm}}{\text{cm}^3}\ 3.55 \times 10^{-8}\ \frac{\text{cm}}{\text{atom}}}{4\ \text{atoms}/(3.55 \times 10^{-8}\ )^3\ \text{cm}^3} \tag{3}$$

or

$$f = 3.15 \times 10^{-4}.$$

Therefore, for the experiment at 470 K, Equation 2 gives

$$C_d = 3.15 \times 10^{-4} C_L \exp\left[4{,}400/1.98\ (473)\right]$$

or

$$C_d = 0.03\ C_L.$$

On substituting into Equation 1,

$$C_T = 1.03\ C_L.$$

Therefore, for a large dislocation density, only a 3% increase is expected in total hydrogen concentration over the well-annealed alloy. The hydrogen measurement capability is not accurate enough to observe this small effect. Therefore, experimental results for Types 304L and 21-6-9 austenitic stainless steels agree with this calculation. Solution-annealed specimens of modified Type A-286 stainless steel had a higher hydrogen concentration than HERFed specimens. This higher concentration suggests that precipitate morphology and volume fraction had a greater influence than dislocation density did on hydrogen solubility.

EFFECTS OF NITROGEN

The hydrogen solubility of Type 21-6-9 stainless steel measured in this study was approximately 40% higher than that of Type 304L stainless steel. This effect is thought to be due to the high nitrogen content (0.1-0.4 wt %) in Type 21-6-9 stainless steel. Nitrogen is added to this alloy as a strengthening alloying element. Tritium solubility of Type 21-6-9 stainless steel measured in another study was about 50% higher than that of Type 304L stainless steel, which agrees with the present result (7).

Binding between nitrogen and hydrogen in the alloy could arise from chemical binding or interaction between strain fields. The chemical binding would be due to the reaction

$$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightarrow NH_3. \qquad (4)$$

However, at 470 K, the free energy for formation of NH_3 is approximately +1,000 cal/mole (5). Therefore, no hydrogen segregation to nitrogen is expected due to chemical binding. However, nitrogen is an effective strengthening alloying element in austenitic stainless steels because of the large strain field that exists around single nitrogen atoms or clusters of nitrogen atoms. Hydrogen will segregate to regions of high tensile lattice strain (6). Therefore, the increase in hydrogen solubility in Type 21-6-9 stainless steel compared to Type 304L stainless steel is probably due to hydrogen segregation into the tensile strain field associated with the nitrogen atoms.

EFFECTS OF SURFACE FINISH

Hydrogen solubility appears to be approximately 8% larger for electropolished surfaces than for ground surfaces when the same thermomechanical treatment is compared. The standard deviation for this variation in solubility was 5%. Variations this small are at the limit of sensitivity of the determination. However, the trend is real as may be seen from the data for Type 304L stainless steel in Table 2. Hydrogen pickup during electropolishing is a possible source of the extra hydrogen but is not expected to be such a large effect.

COMPARISON WITH THE SOLUBILITY DETERMINATIONS FROM PERMEATION MEASUREMENTS

Louthan and Derrick (8) experimentally measured the hydrogen permeation rate in a variety of austenitic stainless steels, including Types 304L and 21-6-9. The hydrogen diffusivity was calculated from the experimental results of rate of rise to steady state. The hydrogen solubility was calculated by dividing the steady state permeation rate by the diffusivity. The hydrogen solubility calculated in this manner includes only the mobile hydrogen that can diffuse through the alloy and none of the irreversibly trapped hydrogen.

As shown in Table 2, the hydrogen solubility calculated from the equation presented by Louthan and Derrick (8) agrees with data for Type 304L stainless steel with all thermomechanical treatments and for annealed specimens of the modified Type A-286 stainless steel. No difference in hydrogen solubility was observed for Types 304L and 21-6-9 stainless steels (8). These observations may be interpreted as showing that there is very little trapping in Type 304L stainless steel and that nitrogen acts as a very effective trap in Type 21-6-9 stainless steel.

TABLE 1

Nominal Compositions of the Austenitic Stainless Steels Studied

	Concentration in Alloy, wt %		
Alloy	304L	21-6-9	A-286
Ni	8.0-12.0	5.5-7.5	29.0-31
Cr	18.0-20	19.0-21.5	13.5-16.0
Mn	2.00 max	8.0-10.0	0.20
C	0.03 max	0.08 max	0.1-0.3
P	0.045 max	0.06 max	
S	0.03 max	0.03 max	
Si	1.00 max	1.00 max	
N		0.15-0.40	
V			2.0-2.3
Al			0.15-0.35
B			0.002 max
Mo			1.0-1.5

TABLE 2

Hydrogen Solubility at 470 K and 69 MPa (10,000 psi)

Alloy	Thermomechanical Treatment	Surface Condition	Hydrogen Concentration, ppm (wt)
304L	Annealed	600, grit	72
		EP, Electropolished	81
	Cold-Worked 100%	600	71
		EP	81
	HERFed	600	71
		EP	79
21-6-9	Annealed	600	118
		EP	126
	Cold-Worked	600	126
		EP	127
	HERFed	600	119
		EP	126
A-286	Annealed	600	80
		EP	81
	HERFed	600	51
		EP	55
Hydrogen Concentration Calculated from Reference 8			79

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