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Abstract

Nickel based alloys are often welded with argon/hydrogen shielding gas mixtures to minimize oxidation and improve weld quality. However, shielding gas mixtures with $\geq 1\%$ hydrogen additions can result in hydrogen concentrations greater than 5 wt. ppm in the weld metal and reduce ductility via hydrogen embrittlement. For the conditions investigated, the degree of hydrogen embrittlement is highly variable between 5 and 14 wt. ppm. Investigation of hydrogen embrittlement of EN82H GTAW welds via tensile testing, light microscopy, transmission electron microscopy, orientation imaging microscopy, and thermal desorption spectroscopy shows that this variability is due to the inhomogeneous microstructure of the welds, the presence of recrystallized grains, and complex residual plastic strains. Specifically, research indicates that high residual strains and hydrogen trapping lower the ductility of Ni-Cr-Mn-Nb weld metal when dissolved hydrogen concentrations are greater than 5 wt. ppm. The inhomogeneous microstructure contains columnar dendritic, cellular dendritic, and recrystallized grains. The decreased tensile ductility observed in embrittled samples is recovered by post weld heat treatments that decrease the bulk hydrogen concentration below 5 wt. ppm.

Background

When welding nickel-based alloys and austenitic stainless steels, shielding gas mixtures of argon and up to 5% hydrogen have been used [1]. Hydrogen additions to argon, make the shielding atmosphere slightly reducing and increases the arc voltage. The reducing environment helps minimize surface oxidation common to nickel-chromium alloys and the increase in arc voltage raises the temperature of the arc. However, hydrogen additions to the shielding gas also increase the likelihood of hydrogen embrittlement. Hydrogen bearing shielding gases are not recommended for many alloys with relatively low hydrogen solubility such as steels, aluminum, and magnesium alloys due to hydrogen gas porosity and the possibility of hydrogen embrittlement [1].

While nickel-based alloys are more resistant to hydrogen embrittlement than many ferritic, bainitic, or martensitic steels, the present work shows that 95%Ar/5% H_2 shielding gas can embrittle Ni-Cr-Mn-Nb welds. Moreover, the relatively slow diffusivity of hydrogen in nickel limits the beneficial effects of hydrogen outgassing during post weld heat treatment so that hydrogen embrittlement or delayed cracking in service must be considered.

Experimental Procedure

Materials Used

The filler wire used was 0.045" diameter Alloy EN82H where "H" denotes a high carbon variant (0.03 wt.% min.) of Alloy EN82. EN82H is the military designation for ERNiCr-3. The nominal composition of EN82H is given in Table 1. In the hydrogen absorption studies, Inconel Alloy 600 was used for the base plate to minimize dilution of the EN82H filler wire.

Table 1. Nominal Composition of Filler Metal EN82H

Ni	Cr	Mn	Nb	Fe	Ti
67.0 min	18.0-22.0	2.5-3.5	2.0-3.0	3.0 max	0.75 max
Si	Cu	C	P	S	Other
0.50 max	0.50 max	0.03- 0.10	0.03 max	0.015 max	0.50 max

Welding Parameters

Multi-pass, automatic gas tungsten arc welding (GTAW) was used in this investigation. For hydrogen uptake measurements, bead-on-plate welds (2 beads wide by 3 beads high) were fabricated with different shielding gas compositions. The welding parameters used for the hydrogen uptake studies are given in Table 2. For mechanical property tests, both EN82H buttering and a heavy section (~2" thick) narrow groove weld were fabricated using the 95%Ar/5% H_2 shielding gas parameters. The buttering was deposited in two different orientations and are referred to as 'Type I' and 'Type II' buttering as shown in Figure 1.

Figure 1. Schematic of the two types of buttering (I and II) and narrow groove (NG) weld investigated in this study.

Shielding gases for the argon/hydrogen combinations were mixed from bulk gas and checked with a gas analyzer. The final shielding mixture was kept within $\pm 0.1\%$ of the specified value. Shielding gas for the helium/argon combination was obtained from a pre-mixed cylinder. Between each bead, the weld was cleaned via wire brushing and visually inspected for any flaws.

Table 2. Summary of AGTAW-Hot Wire Welding Parameters

Shield gas	95Ar/5H ₂	97Ar/3H ₂	99Ar/1H ₂	75He/25Ar
Voltage (Volts)	12.5	12.5	12.5	13
Current (Amps)	300	300	300	290
Travel Speed (in./min.)	6.5	6.5	6.5	8
Osc. Freq. (cyc./min)	85	85	85	85
Osc. Width (inches)	1/2"	1/2"	1/2"	3/16"
Hot Wire Parameters (Volts / Amps)	5.7 / 80	5.8 / 80	5.8 / 80	5.8 / 80
Wire Feed (in./min.)	180	180	180	180

Mechanical Testing

The effect of dissolved hydrogen on the mechanical properties of EN82H welded with 95%Ar/5%H₂ shielding gas was evaluated via uniaxial tensile tests performed at room temperature. The tensile bar diameters were 0.252" and were oriented parallel with the welding direction. The tensile bars were loaded at a rate of 0.005 in./min. until yielding and 0.05 in./min. after yielding until failure. Tensile tests were performed on two types of buttering and on the narrow groove portion of the weld. Hydrogen concentrations were varied via post weld heat treatment at 1050°F for times between 0 and 12 hours.

Microstructural Characterization

Samples for light microscopy were conventionally polished and electrolytically etched in a mixture of 8 parts phosphoric acid to one part water. Both polarized light and Nomarski differential interference contrast (DIC) illumination modes were used to help characterize the microstructure. Scanning electron microscopy (SEM) of tensile bar surfaces was performed on an AMRAY 1830 with a LaB₆ filament. Transmission electron microscopy (TEM) was also performed on selected samples. After sectioning, the TEM foils were mechanically ground and electropolished in a solution of 20% perchloric acid in methanol to achieve electron transparency. The specimens were examined with a Phillips CM 300 microscope operated at 300 keV.

Orientation imaging microscopy (OIM) measurements were performed via electron backscatter diffraction (EBSD). Experimentally, the EBSD pattern is generated when a primary electron beam impinges on the crystalline sample surface. The diffraction pattern is recorded with a phosphor-based detector, converted into a digital signal, and indexed with commercially available software. The instrument used to collect the

diffraction pattern was a CamScan SC44 SEM with a tungsten filament and a Hamamatsu camera and image processor.

Hydrogen Measurements

The hydrogen concentration of the welds fabricated with different shielding gases was measured post-test by sectioning a 0.5"x0.5"x0.01" thick slice from a section near the center of each weld deposit. This location was chosen to minimize the hydrogen loss from regions near a free surface. The samples for hydrogen analysis were at least 0.01" from the face of the last weld bead deposited. The hydrogen concentration of each tensile bar tested was also determined by sectioning a piece of the gage section. Hydrogen concentrations were determined by LECO-type thermal extraction.

In addition to quantitative hydrogen measurements, thermal desorption spectra from the narrow groove weld was obtained at a constant heating rate of 5°C/minute between 25°C and 1000°C. The sample was heated via RF heating in an ultra-high vacuum system, and the hydrogen signal (mass/charge=2) was monitored with a quadrupole mass spectrometer. The resulting data were normalized to the mass of the sample.

Results

Hydrogen Uptake

The as-welded hydrogen concentration for each shielding gas is shown in Figure 2. Note that the hydrogen concentration dissolved in the metal decreases as the hydrogen concentration of the shielding gas decreases. Hydrogen concentrations range from ~12.5 wt. ppm in the 95% Ar/5% H₂ weld to ~3.5 wt. ppm in the 75%He/25%Ar weld.

Figure 2. Comparison of the dissolved hydrogen concentration in EN82H welds as a function of shielding gas.

Mechanical Testing

The tensile data, plotted versus hydrogen concentration, are summarized in Figure 3. Note the large variability in tensile properties both between weld types (Type I buttering, Type II buttering, and the narrow groove weld) as well as within a given weld type. However, one notable trend is the decrease in ductility as the dissolved hydrogen concentration in the metal increases.

Figure 3. Summary plots of tensile data for EN82H as a function of hydrogen concentration. Note that in general, as the internal hydrogen concentration increases, the % elongation, % reduction in area, and the ultimate tensile strength decrease.

Microstructural Characterization

Metallographic investigation of the welds showed three distinct microstructures. Recrystallized grains were observed in limited regions between weld beads as shown in Figures 4a and 5a. Recrystallized grains were readily distinguished under polarized light and occasionally contained annealing twins (Figure 5a). Recrystallization occurred in regions between adjacent weld beads and was observed in both types of buttering and the bead on plate welds used for hydrogen uptake measurements, but not in the narrow groove welds. Cellular dendritic grains were of similar size scale to recrystallized grains as shown in Figure 4b. However, these solidification grain boundaries were more readily distinguished under Nomarski DIC illumination than polarized light. Lastly, the majority of the weld structure was columnar dendritic in nature as shown in Figure 4c.

In general, SEM of tensile bar fracture surfaces showed ductile, microvoid coalescence for high ductility bars (>30% elongation), and interdendritic-type fracture (Figure 5c) for moderate to low ductility tensile bars. Limited regions of intergranular fracture were also noted on several low-ductility tensile bars (Figure 5b). The largest area of recrystallization was calculated to be ~10% of the fracture surface. Bars which exhibited regions of intergranular fracture are denoted by a "+" in Figure 3. Lastly, a relatively brittle, transgranular "quasi-cleavage" type fracture mode (Figure 5d) was also observed in several low ductility tensile bars.

A comparison of TEM images from dendritic and recrystallized regions of a low ductility tensile bar are shown in Figure 6. Figure 6 shows the dislocation structure around (6a) a low angle boundary and (6b) a triple point of recrystallized grains. Figure 6c shows $M_{23}C_6$ -type carbides on an interdendritic boundary.

Thermal Desorption Spectroscopy

A thermal desorption spectra from the narrow groove weld is shown in Figure 7. Data are plotted as the relative intensity of the hydrogen signal vs. temperature. The area under the curve is a measure of the hydrogen concentration. The desorption and binding energies were calculated via Equations (1) and (2) assuming simple de-trapping and diffusion. $E_{Desorption}$ is the desorption energy, R is the gas constant, T_{max} the temperature of the peak maximum, and B is a fitting parameter.

$$E_{Desorption} = R \cdot T_{max} (B \cdot T_{max} - 1) \quad (1)$$

$$E_{Binding}^{Trap\#n} = E_{Desorption}^{Trap\#n} - E_{Desorption}^{Lattice} \quad (2)$$

Orientation Imaging Microscopy

Figure 8 shows the results of orientation imaging microscopy performed on the three regions (type I and type II buttering and the narrow groove weld) from the heavy section welds. The OIM results are compared via the "amis" parameter, which is a measure of the average misorientation between high angle grain boundaries. The "amis" value can be correlated to the residual plastic strain in the weld.

Figure 4. Comparison of the microstructures observed in the welds a.) recrystallized grains b.) cellular-dendritic grains and c.) columnar-dendritic grains.

Discussion

Factors Affecting Hydrogen Embrittlement Resistance

As expected, the degree of ductility loss increases with increasing dissolved hydrogen concentration. However, the data show a large degree of scatter. For example, some tensile bars showed 20% elongation at just below 6 wt. ppm hydrogen while others showed >30% elongation at approximately 13 wt. ppm (Figure 3). Inspection of Figure 3 suggests that the variability in tensile ductility increased as the hydrogen concentration increased. Two factors that likely influence this variability are (1) how hydrogen interacts with the inhomogeneous microstructure of the weld metal, including recrystallized grains and (2) the magnitude and sense of residual stresses and plastic strains.

It is notable that some of the lowest ductility observed occurred on specimens that exhibited some amount of intergranular fracture. Tensile bars that displayed intergranular fracture are denoted by a "+" in Figure 3. When recrystallized grains were

observed, they appeared on 1-10% of the fracture surface. One theory of why recrystallization appears to be detrimental to the hydrogen embrittlement resistance is that recrystallized grains preferentially trap hydrogen, lowering the cohesive strength of the recrystallized grain boundaries. However, TEM examination shows little evidence of intergranular precipitation, which could produce microstructural hydrogen trapping.

Another, more plausible explanation is that the mismatch in strength between recrystallized regions and the dendritic weld metal acts to localize damage in recrystallized regions. During tensile testing, the low-strength recrystallized grains likely deform preferentially and may promote hydrogen localization via the driving force for hydrogen occlusion near regions of high triaxiality. This explanation is consistent with the observed decrease in ultimate tensile strength with increased hydrogen concentration (Figure 3).

Thermal desorption spectra from the narrow groove portion of the weld (Figure 7) shows hydrogen release from possibly four trapping states with peak centers near 230, 330, 420, and 970°C. Assuming that lattice desorption occurs at the same temperature as in wrought nickel and nickel based alloys (~230°C), Equations 1 and 2 can be used to estimate the trap binding energies [2-4]. Assuming simple diffusion and detrapping behavior, the trap state binding energies are estimated to be 24, 50, and 286 kJ/mol as summarized in Table 3.

While additional research is needed to identify the microstructural features associated with each trapping state, the results show that hydrogen-microstructure interactions do exist and may influence the susceptibility of EN82H to hydrogen embrittlement. In previous studies on alloy X-750, incoherent MC-type carbides have been shown to be detrimental to the hydrogen embrittlement resistance [4]. However, in EN82H weld metal, while interdendritic MC-type carbides are present, they do not appear to release hydrogen at the same temperature as in X-750 condition AH (Figure 7). This suggests that the binding energy of hydrogen to MC carbides is different between EN82H weld metal and wrought X-750.

Table 3. Estimated Hydrogen-Trap Binding Energies

Trap State	T @ Peak Max (°C)	E _{Desorption} (kJ/mol)	E _{Binding} (kJ/mol)
#1 (lattice?)	230	53	---
#2	330	77	24
#3	420	103	50
#4	970	339	286

Figure 5. a.) Metallographic cross section of a failed tensile bar showing a band recrystallized grains. Note the presence of (a) annealing twins and (b) secondary cracking between recrystallized grains. Figure 5b.) is the intergranular fracture surface shown in 5a, 5c.) shows the interdendritic fracture mode and 5d.) the low ductility transgranular fracture mode.

Figure 6. Comparison of TEM images Figure 6a.) shows the dislocation structure near a low angle boundary in a region of dendritic microstructure and (b) the dislocation structure near an area of recrystallized grains. Figures 6a.) and 6b.) are from the failed tensile bar shown in Figure 5. Figure 6c.) shows $M_{23}C_6$ -type carbides from an unstrained portion of a narrow groove weld.

Figure 7. Thermal desorption spectra from the EN82H narrow groove weld and Alloy X-750 AH for comparison. Note that multiple trapping states exist in EN82H.

Figure 8. a.) Euler angle image of a region of band of recrystallized grains and b.) the same region filtered by the average misorientation between grains. The dark regions have low misorientation $<1.5^\circ$, and the lighter regions higher misorientation $>1.5^\circ$.

Since the narrow groove weld is highly constrained, residual stresses and strains may contribute to the variability in the mechanical properties. The magnitudes of the residual plastic strains were investigated via electron backscatter diffraction (EBSD) and determined to range between 0 and 15%. The strain measurements are presented separately in these proceedings [5]. The residual plastic strains were quantified via the average grain misorientation (amis) parameter and an experimentally determined calibration curve. Figure 8 illustrates how the amis parameter can be used to spatially map regions of different plastic strain. The Euler angle image and an amis map of residual plastic strain of an unrestrained bead on plate weld are shown in Figures 8a and 8b respectively. The amis map shows that recrystallized regions have lower misorientation (*i.e.* lower dislocation density) than the dendritic region below the recrystallized band.

One significant finding of the amis measurements is that the residual plastic strains vary from near zero in recrystallized grains to $\sim 20\%$ near the root of the narrow groove weld [5]. Moreover, the strain distribution varies nonlinearly from the narrow groove weld to the Type I buttering [5]. These nonlinear plastic strains complicate the mechanical testing where the residual plastic strain (and hence the yield strength) may vary both between regions of the weld (Type I buttering, Type II buttering, and the narrow groove) as well as along the gauge length of a tensile bar.

Conclusions

- The hydrogen concentration of the shielding gas has a significant influence on the as-welded hydrogen concentration of GTAW EN82H welds. In bead-on-plate welds, hydrogen levels ranged from ~ 12.5 wt. ppm (95%Ar/5% H_2) to ~ 3.5 wt. ppm (75%He/25%Ar).
- Multipass EN82H welds can undergo recrystallization and recrystallized grains decrease the resistance of the weld to hydrogen embrittlement. One possible explanation for the detrimental effect of recrystallized grains is that they are lower strength and tend to localize deformation.
- Multiple hydrogen trapping states are observed in EN82H suggesting that hydrogen/ microstructure interactions may influence the hydrogen embrittlement resistance.
- Residual plastic strains are highly variable in the highly constrained weld and range from near 0% in recrystallized regions to $\sim 20\%$ near the root of the narrow groove weld. Residual stresses and plastic strains likely contribute to the observed variability in the hydrogen embrittlement resistance.

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