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Strengthening Hadfield steel welds by nitrogen alloying

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ABSTRACT

Strengthening Hadfield steel weld repairs by introducing nitrogen into the weld region was proven to be feasible via two welding techniques. The first technique required a pure Hadfield steel filler material to be diffusion treated in a high pressure nitrogen gas environment, and subsequently used during tungsten inert gas welding with a pure argon shielding gas. The second technique used a Hadfield steel filler material, and a 10% nitrogen containing argon shielding gas during tungsten inert gas welding. Both techniques increased the yield strength, the hardening rate, and the ultimate strength of the weld region. Using optical microscopy, scanning electron microscopy, and Auger spectroscopy, we determined that the increased strength of the weld region resulted from a combination of nitrogen alloying and microstructural refinement.

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1. Introduction

Hadfield steel is an austenitic manganese steel which possess high wear resistance, high toughness, and high strain hardening rate. These properties have made it successful in industrial applications which include impact hammers, crusher jaws, grinding mill liners, crawler treads for tractors, and railroad frogs.[1] The major alloying components in Hadfield steel include approximately 10–14 wt.% Mn and 1–1.4 wt.% carbon. The high manganese content serves to lower the stacking fault energy, and to raise the solubility for interstitial carbon and nitrogen. The increased solubility of interstitial elements allows for a high carbon concentration without carbide precipitation. Additionally, the high carbon concentration lowers the martensite start temperature which effectively suppresses the martensitic transformation during quenching, and during deformation [1]. This significantly improves the fracture toughness.

Cracks in Hadfield steel railroad frogs are statistically the most probable failure mode in railroad crossings [2]. Frequent maintenance operations cause disruptions in train service which can lead to expensive delay costs [2]. Current weld repairs are known to be weaker than the original casting, and thus subsequent repairs often overlap previous weld repairs [3]. The weld filler material and the welding procedures influence the life of the repaired frog. The frog castings are expensive, and therefore the ability to repair them with stronger welds has economic advantages.

It is well known that adding nitrogen to steel particularly improves its mechanical strength and its corrosion resistance [4,5]. Most of the previous studies on nitrogen alloying (N-alloying) have focused on austenitic stainless steels. Early investigations by Speidel et al. report the yield strength to increase nearly three fold with an addition of 0.8 wt.% nitrogen in solid solution [5]. Additionally, an increase in ultimate strength as a function of nitrogen content has been reported for the 201 stainless steel [6]. They found an increase in tensile strength of approximately 40% for an addition of 1 wt.% N (includes nitrogen in solid-solution and in precipitate form). More recently, the compressive response of nitrogen alloyed single crystal Hadfield steel was investigated [7]. They reported that the compressive yield strength nearly doubled when Hadfield steel alloyed was alloyed with 1 wt.% N. In that previous study, Canadinc et al. determined that large nitrides, approximately 1 μm in diameter, were partially responsible for the increased strength.

Previous research on N-alloying of Hadfield steel is limited to single crystals, and no literature can be found on N-alloying of Hadfield polycrystals or N-alloying during welding of Hadfield steel. In contrast, a significant amount of research is reported on N-alloying during welding of austenitic stainless steels. For instance, Borst et al. added 0.19 wt.% nitrogen to a weld region by use of a nitrogenated filler rod, and found increased tensile strength and increased creep resistance in the weld region [8]. Hertzman et al. have introduced nitrogen into the shielding gas during TIG (tungsten inert gas) welding, and found that nitrogen from the shielding gas diffused into the weld base metal [9,10]. Other researchers have investigated the

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[1] Railroad frogs are railroad components that merge rails.

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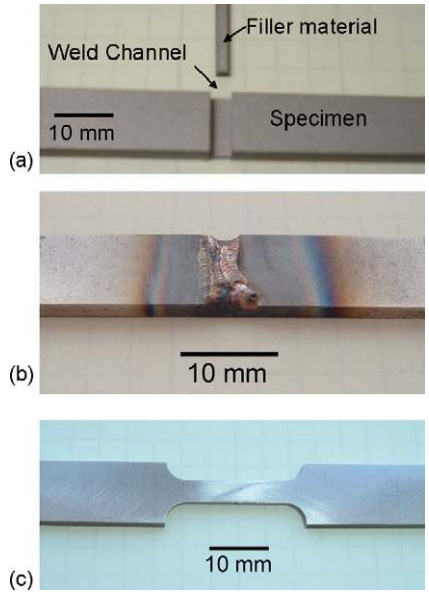

Fig. 1. (a) Geometry of the filler material and the tensile test specimen. (b) Welded specimen. (c) Welded specimen after removal of start–stop effects.

Fig. 2. Miniature extensometer attached to the test specimen.

effect of different nitrogen content in the shielding gas, and have compared N-alloying capabilities of different welding techniques [11,12].

The current investigation focuses on the tensile stress–strain response, the microstructure, and the composition of polycrystals resulting from diffusion treatments, and from welding of Hadfield steel. Increases in the yield strength, the hardening rate, and the ultimate tensile strength are found for the weld region. The increased strength of the Hadfield steel welds are attributed to the increased nitrogen concentration and microstructural refinement.

2. Materials and methods

The Hadfield steel used in this study was electro-discharge machined from a virgin railroad frog supplied by David Davis at Transportation Technology Center Incorporated in Pueblo, Colorado. The specimen and filler metal geometry are shown in Fig. 1(a). The cross-sectional dimensions of the weld specimen were approximately 3 mm × 10 mm. A 3.2-mm wide weld channel was machined to approximately 90% of the specimen thickness to preserve specimen alignment during welding. A Lincoln Electric Square Wave TIG 255 was utilized to perform all TIG welds. Welding conditions used for all welds were approximately 20 A and 10 V, and a shielding gas pressure of 12 PSI. All experiments were conducted at the University of Illinois at Urbana-Champaign.

Diffusion treatments for the N-alloyed Hadfield steel filler material were conducted in a 17 kPSI nitrogen environment at 1200 °C, or 1275 ° C for 5 h. These treatments yielded a bulk nitrogen concentration of 0.75 and 1.02 wt.% respectively in the diffusion treated filler material (shown in Table 1). Bulk nitrogen content of the virgin Hadfield steel, and the diffusion treated samples was determined by inert gas fusion-thermal conductivity. The bulk measurements were conduced by IMR test labs in Lansing, NY.

Table 1
Bulk nitrogen concentration in wt.% for the virgin Hadfield steel, and for the diffusion treated Hadfield steel at 1200 ° C and 1275 °C.

Hadfield steel	1200 °C	1275 °C
N	0.75	1.02

For the first welding technique, a diffusion treated filler metal was utilized during TIG welding with a pure argon shielding gas. In contrast, the second welding technique did not use a diffusion treated filler metal or pure argon shielding gas. The second welding technique used a pure Hadfield steel filler metal, and a shielding gas that had approximately 90% Ar and 10% N. Once the test samples were welded (shown in Fig. 1(b)), the start–stop effects were removed by water jet machining which also introduced a dog-bone shaped gauge section (shown in Fig. 1(c)). The top and bottom surfaces were subsequently ground and polished with 320 grit paper resulting in a cross-section of approximately 2 mm × 4 mm for tensile testing. This also accommodated the use a miniature extensometer.

Table 2
The primary peak energy used to identify the element, and the elemental sensitivity used to calculate the composition.

	C	N	O	Mn	Fe
Peak energy (eV)	272	379	503	542	703
Elemental sensitivity	0.128	0.246	0.296	0.173	0.246

Note that the sensitivities are relative to a Ag calibration standard.

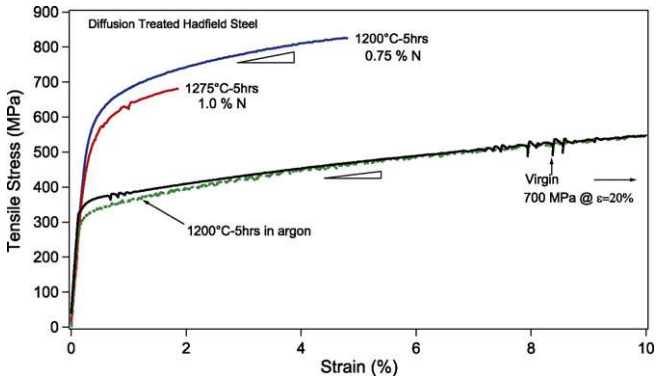

Fig. 3. Tensile behavior of the virgin Hadfield steel, the diffusion treated Hadfield steel, and the Hadfield steel treated in argon.

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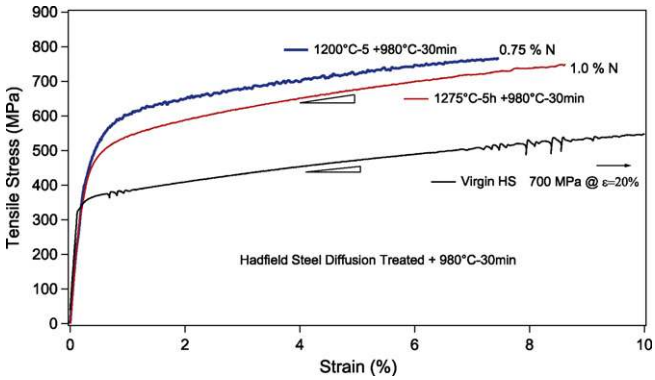

Fig. 4. Stress–strain response of the diffusion treated Hadfield steel after a short austenitizing treatment. Note the virgin Hadfield steel curve is repeated from Fig. 3 for comparison.

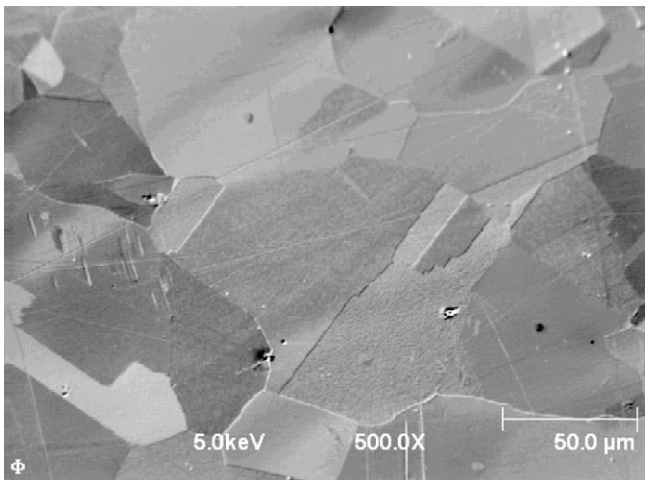

Fig. 6. Scanning electron micrograph of the Hadfield steel after electro-polishing and sputter cleaning.

The tensile tests were conducted in an 80 kN load capacity MTS servohydraulic frame with hydraulic grips. Strain was measured in the welded region with a miniature MTS extensometer with a 3 mm gauge section (shown in Fig. 2). The extensometer gauge length was approximately the dimension of the weld "channel" so that the measurements were representative of the weld material. The specimens were loaded to failure in displacement control which resulted in a strain rate of approximately 10^{-3}/s.

To help identify the origin of the increased strength, microstructural features such as grain size and shape, and the presence of other phases were investigated by optical microscopy, and scanning electron microscopy. Sample preparation for microscopic investigations included grinding, and mechanical polishing with 800 grit paper. Some samples were subsequently electro-polished in Nital to remove any deformed layer resulting from the polishing process. The use of Nital as an electrolyte also etches the material which reveals the grain boundaries and second phases.

In addition to characterizing the microstructural features, composition differences of microstructural features were investigated utilizing Auger spectroscopy. Auger spectroscopy is primarily a surface analysis technique which is highly sensitive to light elements. Initial data of the specimen surfaces had significant oxidation from either the environment or the electrolyte. Ion milling was performed in vacuum prior to subsequent surveys to remove any surface contamination.

All surveys were obtained with a primary electron beam voltage of 5 keV. A quantitative analysis of the chemistry involves a comparison of peak-heights of each element from the Auger spectrum. In addition, each element has a relative sensitivity factor which is ideally measured off of a calibration standard that has a similar matrix chemistry to the "test" sample. Unfortunately, a calibration standard was not available for the Hadfield steel. The alternative method utilizes a Ag calibration standard. The relative elemental sensitivities and the peak energies which were used to determine them are listed in Table 2. Details about converting peak-heights to quantitative composition measurements using elemental sensitivities can be found in Ref. [13]. Iron and manganese each have three primary peaks in the high energy transition which can be selected to determine the elemental sensitivity and the composition (542 eV, 589 eV and 636 eV for Mn, and 598 eV, 651 eV and 703 eV for Fe). Normally the second peak is chosen for Mn at 589 eV, but since it overlaps with the first iron peak we chose the 542 eV for Mn and the 703 eV for Fe. The choice of which peak to use can influence the *quantitative* estimate of the elemental sensitivity and the composition, but since the peak selection is the same for all Auger surveys, the *qualitative* estimates are not affected. Thus Auger spectroscopy is useful for identifying enrichments/depletions in elements, and the spatial distribution of elements in regions as small as 0.5 µm × 0.5 µm.

3. Results

3.1. Mechanical experiments

Typical stress–strain curves of the Hadfield steel, and the diffusion treated Hadfield steel are shown in Fig. 3. An increase of

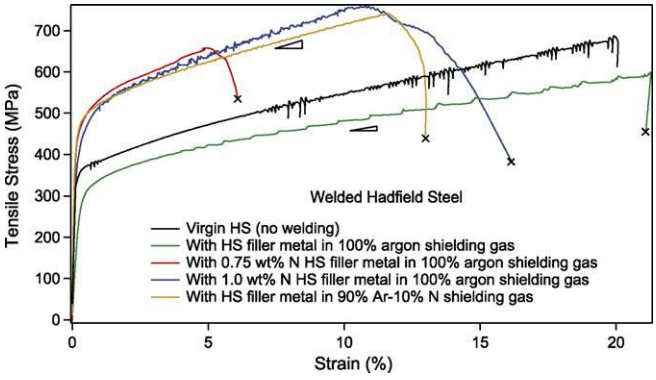

Fig. 5. Stress–strain response of the welded Hadfield steel specimens. Note the virgin Hadfield steel stress–strain curve is repeated from Fig. 3.

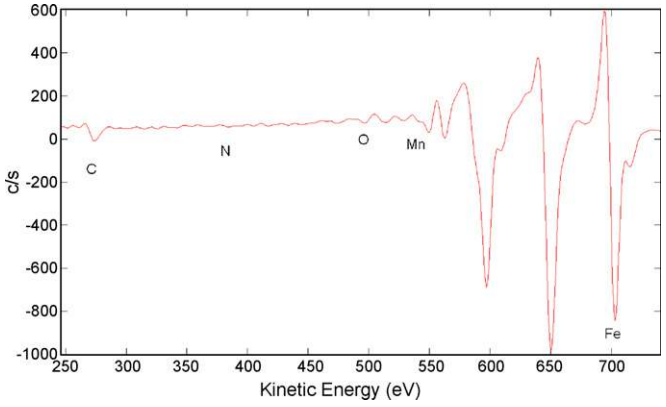

Fig. 7. Auger spectrum of the virgin Hadfield steel. Note that no peak is detected for nitrogen at a kinetic energy of 379 eV.

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Table 3
Concentration of alloying elements calculated from the Auger spectrum for the virgin Hadfield steel (in wt.%).

	C	N	O	Mn	Fe
Matrix	2.2	0.2	0.6	2.9	94.0

Note that these concentrations will be compared to that measured in the diffusion treated and welded microstructures so that enrichments/depletions can be identified.

approximately 80% in the yield strength, and 70% in the hardening rate was found for the diffusion treated Hadfield steel. Since the diffusion process is conducted at high temperatures, grain growth may alter the mechanical properties, and to determine this effect, a specimen was treated in argon at 1200 ° C to quantify the expected decrease in strength (see the "1200 °C–5 h in argon" stress–strain curve in Fig. 3). No substantial change in properties was found due to grain growth or other effects of the heat treatment. Comparison of grain sizes from optical micrographs of the virgin and the diffusion treated samples revealed minimal grain growth. The ductility of the diffusion treated Hadfield steel decreased considerably, but some ductility could be regained by a short austenitizing treatment as is shown in Fig. 4. The short austenitizing treatment did not alter the bulk nitrogen concentrations.

The tensile stress–strain curves of the welded Hadfield steel samples are shown in Fig. 5. An increase of approximately 60 % in yield strength, 70% in the hardening rate, and 25% in ultimate strength is found for both welding techniques. Note that welding with either 1.0 or 0.75 wt.% N containing Hadfield steel filler material resulted in approximately the same yield strength. Also shown in this figure is the virgin Hadfield steel curve from Fig. 3, and one specimen that was welded with virgin Hadfield steel filler material for a weld-baseline comparison.

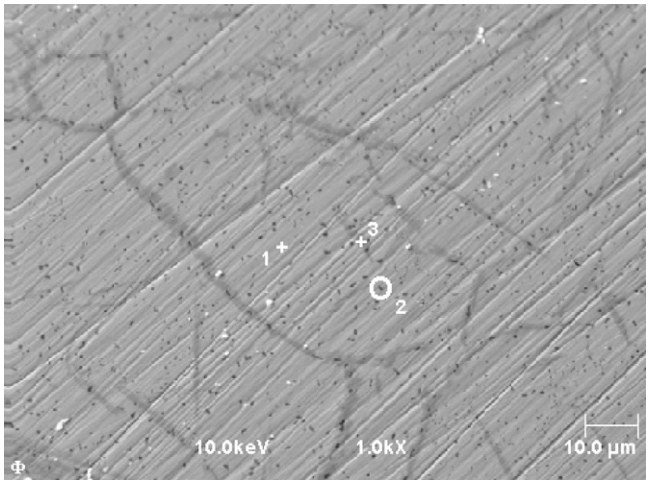

Fig. 8. Scanning electron micrograph of the diffusion treated filler metal which was treated at 1275 °C. Point 1 corresponds to the matrix, point 2 corresponds to a precipitate, and point 3 corresponds to a grain boundary. The concentrations are listed in Table 4.

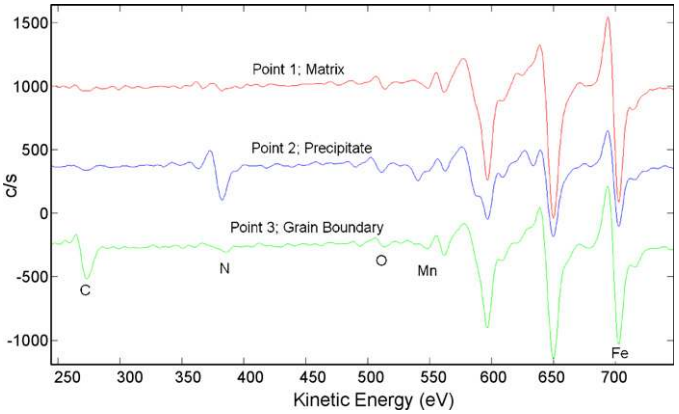

Fig. 9. Auger spectra for the diffusion treated Hadfield steel at 1275 °C.

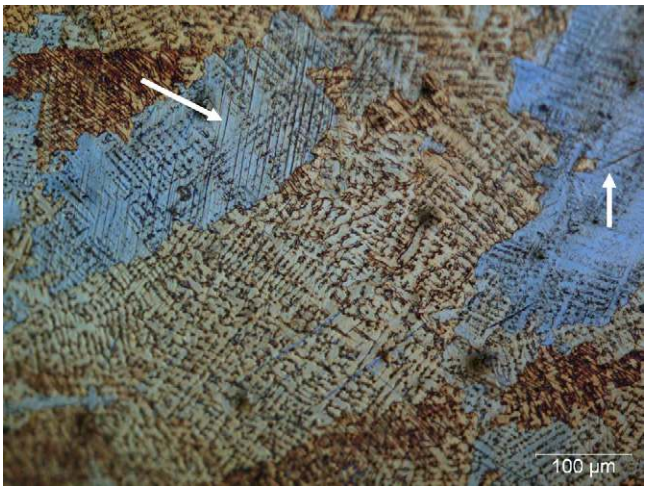

Fig. 10. Optical micrograph of the weld region showing large tinted grains, and a cellular network. Arrows point to twins.

3.2. Microscopy

Fig. 6 displays the typical microstructure of the virgin Hadfield steel obtained from the railroad frog. It is completely austenitic without any precipitates. The grain size varies from 25 to 150 µm. Fig. 7 shows a typical Auger spectrum of the virgin Hadfield steel material. In Fig. 7, the kinetic energy (*x*-axis) identifies the element while the peak height (*y*-axis) indicates the atomic proportion of that element. Quantification is sometimes difficult due to background noise and different elemental sensitivities. Therefore the differences in concentrations of the virgin, diffusion treated, and welded specimens will be used to identify enrichments/depletions of elements in selected microstructural features. The atomic concentrations were normalized to 100%, and then converted to weight percent. Table 3 shows the measurements for the virgin Hadfield

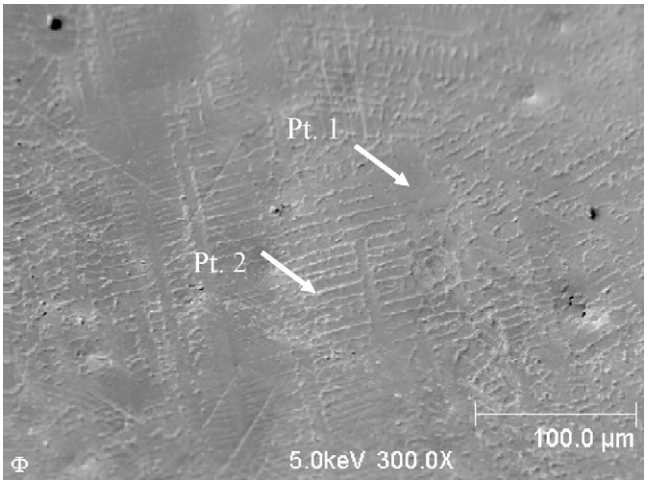

Fig. 11. Scanning electron micrograph of the weld region prior to loading: indicating the two regions analyzed by Auger spectroscopy. Point 1 corresponds to the matrix and point 2 corresponds the ridge feature.

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Table 4
Concentration of alloying elements calculated from the Auger spectra for the filler metal diffusion treated at 1275 ° C (in wt.%).

	C	N	O	Mn	Fe
Matrix (Pt. 1):	1.2	0.9	1.6	1.6	94.7
Precipitate (Pt. 2):	1.4	9.0	2.6	16.3	70.7
Grain boundary (Pt. 3):	9.8	0.8	1.2	2.9	85.3

It is useful to compare these concentrations to those of the virgin Hadfield steel shown in Table 3.

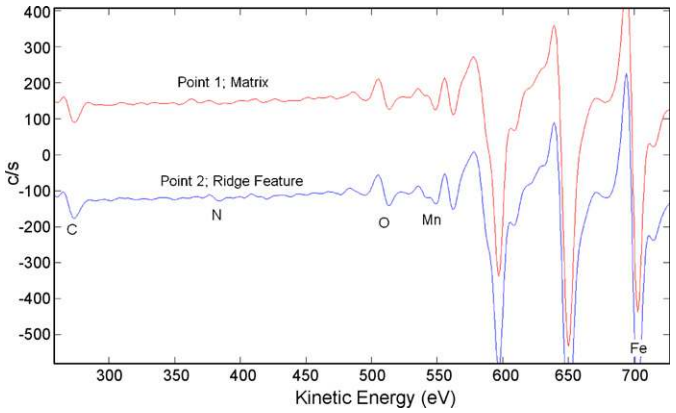

Fig. 12. Auger spectra for the Hadfield steel welded with a 10% N–90% Ar shielding gas.

steel. Note that no peak was detected near 379 eV (the kinetic energy of nitrogen), only background noise was measured in the virgin Hadfield steel (see Fig. 7). Thus, the reported nitrogen concentration in Table 3 suggests a detection level of 0.2 wt.% for nitrogen in Hadfield steel.

A representative micrograph of the diffusion treated filler metal is shown in Fig. 8. Note that precipitates and wide grain boundaries appear in this microstructure which were not present in the virgin material. Utilizing Auger spectroscopy, we determined the compositional differences in the matrix, precipitate, and grain boundary regions. These regions are identified as points 1, 2 and 3 in Fig. 8, and the corresponding spectrum are shown in Fig. 9. The gray region which decorates the grain boundaries (point 3 in Fig. 8) was determined by Auger spectroscopy to be predominantly iron carbide, whereas the black precipitates (point 2 in Fig. 8) are identified as nitrides. Table 4 shows the concentrations of the elements identified by Auger spectroscopy for all three regions. It should be noted that all three regions have a significant nitrogen content, but the nitrides have nearly an order of magnitude more nitrogen.

After welding with the nitrogen containing shielding gas (the second welding technique), the grain size and shape is found to vary within weld region. A representative optical micrograph of the morphology of the welded region is shown in Fig. 10. Note the dendritic appearance which seems to subdivide the grains into a fine network, and what appears to be twins (arrows pointing to thin straight black lines). Fig. 11 shows the matrix region and the ridge feature which was probed by Auger spectroscopy. The Auger spectrum for the matrix and the ridge like features are shown in Fig. 12, and the corresponding concentrations are indicated in Table 5. Note that the two regions analyzed differ only in nitrogen concentration, namely, the matrix region (point 1) has a lower nitrogen concentration than the ridge feature. Also, no nitrides were found in the weld region. Samples which were welded with nitrogen containing filler rod in pure argon shielding gas displayed a similar microstructure although with a smaller average grain size.

Table 5
Concentration of alloying elements calculated from the Auger spectrum in the weld region (in wt.%).

	C	N	O	Mn	Fe
Matrix (Pt. 1):	2.9	0.2	2.0	2.6	90.1
Ridge feature (Pt. 2):	2.9	0.4	2.0	4.5	92.2

It is useful to compare these concentrations to those of the virgin Hadfield steel shown in Table 3.

4. Discussion and concluding remarks

The results of the tensile experiments for the diffusion treated samples showed increases in the yield strength and the hardening rate (Fig. 3). We speculate that the increased yield strength of the diffusion treated material is a combination of nitride precipitates, and nitrogen in solid solution. In contrast to these increases, the ductility decreased. The reduced ductility is likely caused by the iron carbide which decorates the grain boundaries. This reduced ductility was not observed under compressive loads in the previous study by Canadinc et al. where single crystal Hadfield steel was alloyed with nitrogen [7].

In welded specimens, the experiments showed increases in yield strength, hardening rate, and ultimate strength levels (Fig. 5). We determined the increased yield and ultimate strength was attributed to nitrogen in solid solution and a refined microstructure. The low nitrogen concentration of the solidified weld region is not surprising since previous studies of FeCr alloys have shown that nitrogen has a low solubility limit in the molten state [14]. The lower solubility limit in the molten state as compared to the solid state may explain the similar yield strength observed for samples welded with 0.75 or 1.0 wt.% N containing Hadfield steel filler metal (Fig. 5). The optical micrograph of the weld region (Fig. 10) shows a fine network which appears similar to reports for the solidified microstructure of nitrogen alloyed 301 stainless steel with concentrations of 0.35 and 0.65 wt.% [12]. The lack of iron carbide in the weld region and the refinement of the microstructure (Fig. 10) is expected to contribute to the increased ductility compared to the diffusion treated material. The large variability of the ductility found for the welded samples is expected to result from internal flaws generated during weld passes. A preliminary attempt (not reported here) to circumvent the process of filling the weld channel, to eliminate the affect of potential flaws, indicates that sufficient localized heating by striking an arc with the TIG torch with a 10% N containing shielding gas also results in increased strength levels. This preliminary result suggests a potential surface nitriding treatment could be developed based on nitrogen containing shielding gas and conventional welding equipment.

More investigations are needed to determine the optimal nitrogen content in solid solution after welding. Important welding parameters such as heat input, arc distance, nitrogen content of the shielding gas etc. are expected to alter the nitrogen content of the weld region [9,11,12]. Furthermore, optimizing the composition of the filler metal may prove beneficial. For example, welding with stainless steel filler metal (high in Cr and Mn contents) may increase the nitrogen solubility. This may also be advantageous if the severe reduction in ductility is partly due to precipitate formation. Previous studies of nitrogen alloyed stainless steels showed that strengthening attributed to nitrogen in solid solution did not compromise the ductility [15].

In summary, the diffusion treatments were demonstrated to be amenable to the manufacture of welding filler material. The subsequent use of the filler material during TIG welding was shown to increase the strength of the weld region. It is expected that the filler material could be covered with a flux and then used during conventional arc welding for large weld repairs in railroad applications. It was also demonstrated that the addition of nitrogen in the shielding gas would result in diffusion of nitrogen into the weld region

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and provide increased strength. This modification of the shielding gas could be implemented during metallic inert gas welding or TIG welding for strengthening weld repairs or for surface hardening treatments.

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