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Roll-bonded nitrogenated 201 stainless steel

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An alternative to high-pressure melting was used to produce sheets of high-nitrogen stainless steel. Hot isostatic pressure diffusion of nitrogen into thin sheets of 201 stainless steel resulted in enhanced nitrogen concentrations unobtainable in commercial grade stainless steels. Several different nitrogen enhancement techniques were attempted. Hot roll-bonding was then used to produce thick laminates. The resulting tensile strengths were dependent upon the nitrogen concentration of the laminates and were similar to the tensile strength obtained for high-pressure melted nitrogen stainless steels.

1. Introduction

Roll-bonding was used to form laminates from sheets of high-pressure, high-temperature nitrogenated 201 stainless steel (201SS). High-pressure diffusion resulted in nitrogen concentrations not now available in commercial-grade 201SS. Hot-rolling was used to bond the nitrogenated sheets together. The tensile strength of the roll-bonded laminates increased with increasing nitrogen concentrations. Processing techniques used in this study were designed to be consistent with currently available commercial facilities.

Nitrogen addition to stainless steels is known to improve mechanical properties [1–7]. The tensile strength of 201SS is higher than the tensile strengths of 300 series stainless steels which have nitrogen concentrations under 0.1 wt % [8]. The alloy composition of 201SS was specially designed to have a maximum nitrogen solubility of 0.25 wt %. The nitrogen concentration in most stainless steels is limited to the nitrogen solubility the alloy can develop in its molten state, which is lower than nitrogen solubility in the solid state [9, 10].

The nitrogen concentration in most fcc-iron alloys can be increased by solid state diffusion [10–12]. Surface nitriding is a common practice to enhance the nitrogen concentration in the surface region of iron alloys, generally to improve surface hardness. Thus, while nitrogen diffusion has been used to improve surface properties, increasing the bulk nitrogen concentration by surface diffusion is impractical due to economics and time limitations.

With the advent of large commercial hot isostatic pressing (HIP) furnaces (i.e. 1.5 m diameter by 2.25 m high, maximum temperature 1300 °C and pressures in excess of 100 MPa) it is now possible to use high pressures and elevated temperature to diffuse nitrogen into large rolls of sheet metal. Elevated pressures are used because nitrogen solubility in stainless steels is roughly proportional to the square root of the applied pressure [10, 13, 14]. Hot-rolling is used to bond together thin sheets of steel to form a laminate structure. Roll-bonding clads the bulk metal with a surface layer to provide the inner metal protection from the surface environment. The outer material may be selected for improved wear, corrosion, oxidation, or fracture properties.

2. Experimental procedure

In this study, sheets of low nitrogen 201 stainless steel with two different carbon levels (Table I) were nitrogenated in a HIP furnace and then roll bonded. Several different nitriding conditions were employed and several different lay-ups of nitrogenated steel sheets were roll bonded. Hot roll-bonding produced a final laminate product with bulk nitrogen concentrations determined from the diffused nitrogen of the individual thin sheets.

Three different HIP furnace nitriding conditions (temperature, pressure, and time) were studied (Table II). Temperatures were selected to be as high as practical (1000–1250 °C) to maximize the diffusion rate. Two different processing times were selected: 15 and 60 min. The shorter time was selected to develop only a limited surface nitrogenated condition. The longer time was selected to allow the nitrogen to diffuse entirely through the sheet resulting in an approximately uniform nitrogen concentration. Two nitrogen pressures (approximately 4 and 10 MPa) were selected to enhance the nitrogen concentration yet ensuring that nitrogen concentration would not exceed nitrogen solubility and produce nitride precipitates.

For each alloy-composition, five different sheet (1.21 mm thick × 150 mm × 100 mm) lay-ups were prepared for roll-bonding (Table III): one lay-up of each of the three different processing conditions, one of the as-received sheets and the fifth a mixture of the "fully" nitrogenated and as-received sheets. For the four like-composition lay-ups, four sheets were used. For the fifth mixed layer lay-up, five sheets were used. The outer and centre layers were "fully" nitride sheets,

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TABLE I Sheets of low nitrogen 201 stainless steel with two different carbon levels

Alloy	Alloy composition							
	Cr	Mn	Ni	Si	Cu	C	N	Fe
T201	16.6	7.12	4.87	0.48	0.74	0.078	0.067	Bal.
T201L	16.9	6.78	3.81	0.37	0.44	0.026	0.15	Bal.

TABLE II High-pressure, high-temperature, nitrogenation processing conditions

	Temperature (°C)	Time (min)	Pressure (MPa)
(a)	1000	15	4.3
(b)	1000	15	11.0
(c)	1250	60	10.0

TABLE III Sample designation

LC1 and HC1[a]	Processing condition[b] (c)	Fully nitrogenated
LC2 and HC2	Processing condition (c)	Mixed and as-received
LC3 and HC3	Processing condition (b)	Surface nitrogenation
LC4 and HC4	Processing condition (a)	Surface nitrogenation
LC5 and HC5		As-received

[a] LCx low-carbon alloy. HCx high-carbon alloy.
[b] Processing conditions see Table II.

the inner layers were as-received sheets. Prior to hot-rolling, the surface of all sheets were sand blasted to remove any surface oxides. To minimize oxidation during heating, the sheets were welded together.

Hot-rolling was accomplished by preheating the welded lay-ups to 1100 °C for 15 min. Two reductions were made. The rollers were set each time for a 50% reduction. Between rollings, samples were again placed in the furnace for 5 min. The second hot-rolling was perpendicular (cross rolled) to the first. To allow comparison with commercial grade annealed tensile data after hot-rolling, the samples were placed back into the furnace and annealed for 1 h.

3. Results and discussion

Microstructural examination of the roll-bonded samples using scanning electron microscopy (SEM) showed that the final grain microstructure for all samples was equiaxed and approximately 30–50 µm diameter. Grain growth occurred across the lamina interfaces indicating a well-bonded material. However, with increasing nitrogen concentration an increasing amount of porosity occurred in the region of the previous sheet interface. The observed porosity was not confined to the interface but was spread out over an area approximately 10–15 µm on either side of the interface (Fig. 1). Because the pores are only observed with increased nitrogen materials, they are believed to result from nitrogen gas coming out of the solution.

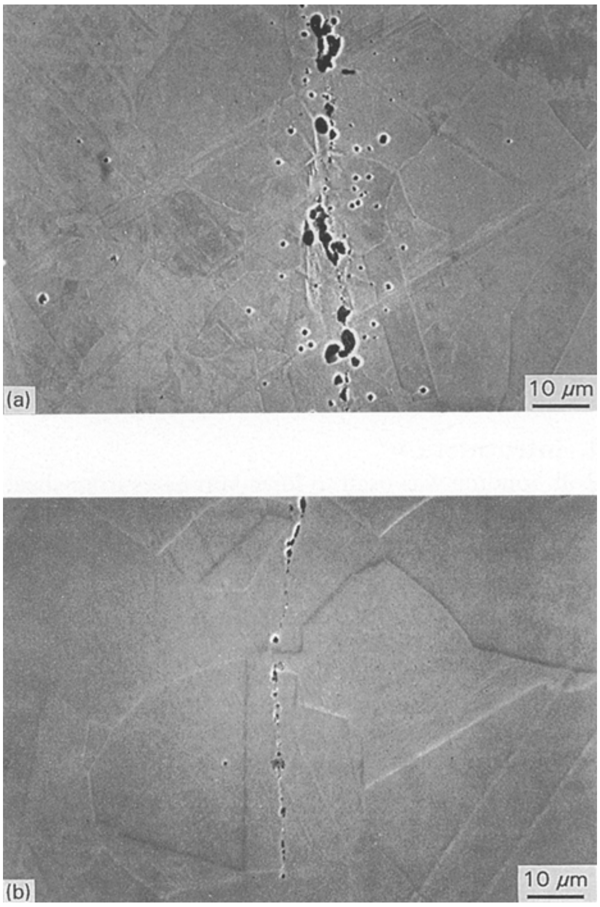

Figure 1 Scanning electron microscopic photograph of high carbon 201 alloy laminated interface. Individual high-pressure, high-temperature sheets were hot-roll bonded. Grain growth was observed between sheets extending across the former interface. Porosity was observed at the former interface. (a) Sample HCl. (b) Sample HC4.

Five tensile samples were cut from each of the roll-bonded samples. Tensile results are presented in Table IV. Metallographical sections were cut from the tensile grip section for nitrogen analysis and scanning electron microscopic examination. In addition, microhardness values were taken across the sample, and microprobe analysis was obtained from the area next to each of the hardness measurements.

Fig. 2 shows that the tensile properties are strongly correlated to the total nitrogen concentration. These results are consistent with results previously obtained by one of the authors when nitrogenated stainless sheets were forged together [11]. Linear regression analysis of the tensile data versus the different total nitrogen/carbon analysis in Table IV are shown in Table V. Tensile properties are proportional to the

TABLE IV Tensile results

	Yield (MPa)	Tensile (MPa)	Elongation[a] (%)	Nitrogen carbon (wt %)
LC1	465 ± 21.3	798 ± 2.4	70 ± 14.0	0.57/0.06
HC1	577 ± 1.0	897 ± 7.5	63 ± 3.5	0.58/0.12
LC2	373 ± 5.5	805 ± 9.1	71	0.33/0.04
HC2	460 ± 10.0	863 ± 0.5	22 ± 1.0	0.53/0.10
LC3	338 ± 3.5	795 ± 1.1	85 ± 2.1	0.23/0.03
HC3	343 ± 6.4	805 ± 5.7	78 ± 2.8	0.24/0.08
LC4	308 ± 4.9	707 ± 4.5	72 ± 3.0	0.16/0.03
HC4	295 ± 11.3	711 ± 2.1	79 ± 4.9	0.09/0.08
LC5	302 ± 3.5	727 ± 4.9	68 ± 1.4	0.15/0.02
HC5	265 ± 3.5	726 ± 2.1	85 ± 0.2	0.07/0.07
[8]	310	655	40	0.25/0.15

[a] Per cent elongation over 30 mm gauge length.

[b] Sample designation from Table III.

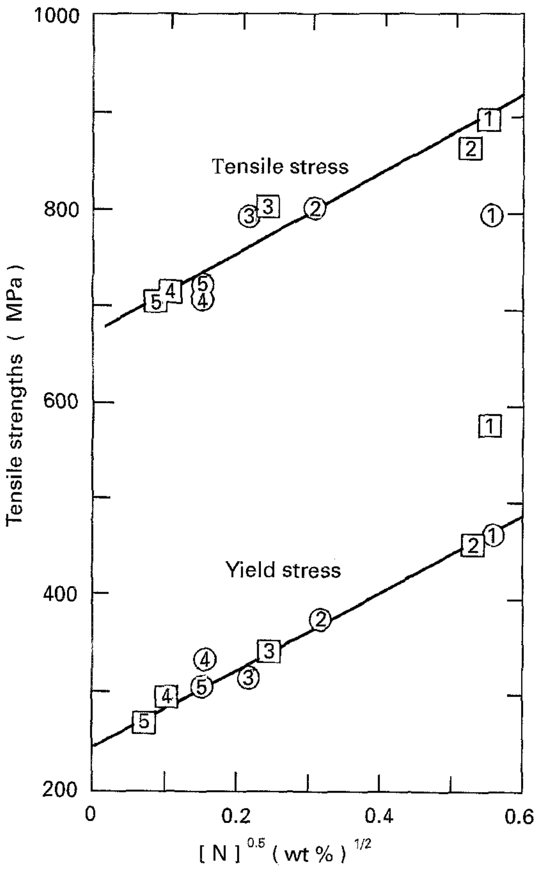

Figure 2 Yield and tensile strength versus the measured total nitrogen concentration. (○) LC, (□) HC.

TABLE V Statistical correlations between tensile properties and nitrogen/carbon concentration ([X] wt %). Statistical data fit characterized by R^2 value

Yield strength (MPa)	
$\sigma^{\text{Y.S.}} = 157 + 395[\text{N}]^{1/2}$	$R^2 = 0.93$
$= 143 + 385[\text{N}]^{1/2} + 332[\text{C}]$	$= 0.94$
$= 242 + 378[\text{N}] + 132[\text{C}]$	$= 0.95$
$= 127 + 307[\text{N}]^{1/2}$ [3]	
Tensile strength (MPa)	
$\sigma^{\text{T.S.}} = 600 + 373[\text{N}]^{1/2}$	$R^2 = 0.90$
$= 587 + 332[\text{N}]^{1/2} + 399[\text{C}]$	$= 0.92$
$= 681 + 335[\text{N}] + 182[\text{C}]$	$= 0.91$

square root of the measured average nitrogen concentration [3, 11]. Analysis of tensile results shows that an atom of nitrogen has twice the strengthening potential as does an atom of carbon. This is important because, while carbon solubility in stainless steels is less than 0.1 wt %, nitrogen has a solubility limit that exceeds 0.6 wt % in many stainless steels.

Increasing the nitrogen concentration increased the tensile properties while not adversely affecting ductility. Thus, it is reasonable to expect the fracture toughness of these roll-bonded materials to increase with increasing nitrogen concentration.

SEM examination showed that the fracture surface of samples with higher nitrogen concentration delaminated. Delamination was observed to occur during the tensile test for those samples that contained the fully nitrogenated sheets, after the samples had reached their tensile strength. The amount of delamination increased with increasing nitrogen concentration.

Microprobe analysis showed that the nitrogen concentration for the as-received and the fully nitrogenated samples were uniform across the entire sample. The nitrogen concentration of the surface nitrogenated sheets did show a slight increase in nitrogen concentration at the bonded interface. The nitrogen concentration of the mixed lay-up showed that there was little diffusion of nitrogen between the different sheets. For the low carbon starting alloy, the inner layers still had a composition close to the as-received nitrogen concentration (0.158 ± 0.084 wt %), and the fully nitrogenated sheets had a nitrogen level near that measured for the fully nitrogenated sheets (0.313 ± 0.063 wt %).

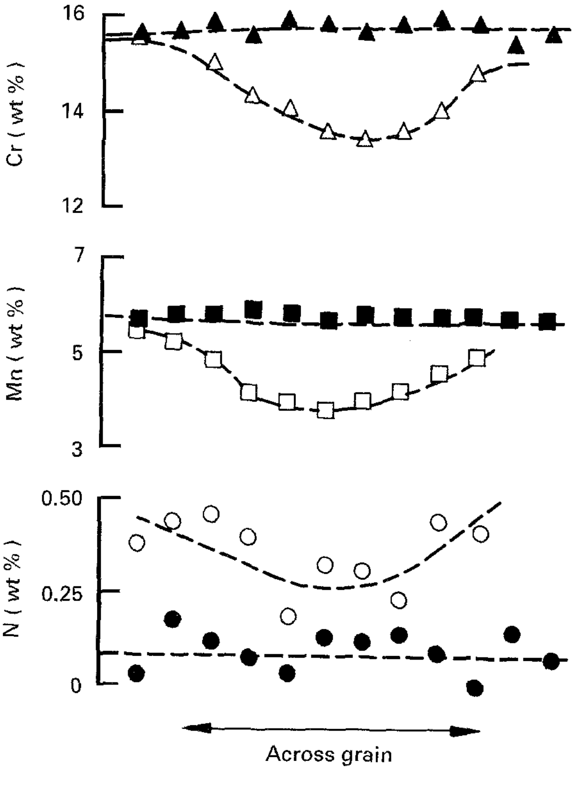

Figure 3 Microprobe analysis across two grains: (△, □, ○) centre of as-received layer; (▲, ■, ●) across the interface of fully nitrogenated sheets.

Several microprobe scans were made across individual grains. Fig. 3 shows that the chromium and manganese concentrations were uniform for the as-received samples. However, for grains that grew across the sheet interface of the fully nitrogenated sample, there was a significant decrease in chromium and manganese concentration in the centre of the grain. This decrease in chromium and manganese concentration at the previous sheet interface would result in a reduced nitrogen solubility and might account for the presence of the observed porosity at the sheet interface cited above.

Nitrogen concentration levels determined by the microprobe are significantly lower than the level determined by the LECO fusion gas technique for the fully nitrogenated sample. The lower nitrogen measured in the metal matrix may be associated with the appearance of porosity at the sheet interface mentioned above.

4. Conclusion

High-pressure, high-temperature nitrogen diffusion is a technique that resulted in nitrogen concentrations in finished stainless steel laminate structures that previously have only been obtained by expensive high-pressure melting. Nitrogenated 201 stainless steel sheets were roll-bonded resulting in uniformly distributed nitrogen concentrations. Tensile properties of the annealed, roll-bonded material were proportional to the nitrogen concentration. Increasing the nitrogen concentration to approximately 0.5 wt % increased the yield and tensile strengths by approximately 200 MPa. Thus, surface diffusion and roll-binding resulted in a rapid and economically viable technique for increasing tensile properties of stainless steels.

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