Nitrogen Desorption by High-Nitrogen Steel Weld Metal during CO_2 Laser Welding

WEI DONG, HIROYUKI KOKAWA, SUSUMU TSUKAMOTO, and YUTAKA S. SATO

Nitrogen desorption by high-nitrogen steels (HNSs) containing 0.32 and 0.53 pct nitrogen during CO_2 laser welding in an Ar-N_2 gas mixture was investigated and the obtained data were compared with those for arc welding and at the equilibrium state predicted by Sieverts' Law. Although the nitrogen content in the weld metal during CO_2 laser welding was lower than that in the as-received base material in all conditions, the nitrogen desorption was larger in the top part of the weld metal than in the keyhole region. The nitrogen desorption in the Ar atmosphere was less during CO_2 laser welding than during arc welding. With the increase in nitrogen partial pressure, the nitrogen content in the weld metal sharply increased during arc welding, but only slightly increased during CO_2 laser welding. The nitrogen absorption and desorption of the HNS weld metal were much smaller during CO_2 laser welding than during arc welding.

I. INTRODUCTION

THE gradual recognition during the second half of the last century of the beneficial effects of nitrogen on the properties of high-alloy steel, such as strength, corrosion resistance, austenite stability, *etc*., led to the widespread development of high-nitrogen steels (HNSs), as demonstrated in numerous applications.[1–4] However, an exchange of the intentionally raised nitrogen with the atmosphere due to alloying or to pressure and powder metallurgy is quite likely to occur, resulting in porosity and detrimental changes in properties during fusion welding. Although pressure welding processes such as flash-butt welding are not considered to be problematic with respect to nitrogen, the limitations of these welding methods and the usual precautions necessitated by the use of high-nitrogen alloy materials must be taken into account.[5] To establish a suitable welding method for HNSs, it is essential to investigate the nitrogen absorption and desorption of the weld metal during the welding of HNSs.

The behavior of nitrogen in weld metals of iron and stainless steels with low-nitrogen contents during arc welding has been extensively investigated.[6–21] The results of such investigations show that the nitrogen absorption by the weld metal is enhanced above the equilibrium solubility of nitrogen predicted by Sieverts' Law and that the existence of monatomic nitrogen dissociated from molecular nitrogen in the plasma is responsible for the enhancement of the nitrogen absorption in the low-nitrogen steel weld pool during arc welding.

Laser welding has recently received increasing attention due to its high energy density and low heat input as compared with conventional fusion techniques. Laser welding is expected to have a great impact on fabrication and manufacturing industries in the welding of steel structures within the next decade. Previous studies have shown that the nitrogen content in iron and stainless steels with a low-nitrogen-content weld metal during CO_2 laser welding is higher than during the neodymium:yttrium aluminum garnet (Nd:YAG) solid-state laser welding, but lower than during gas tungsten-arc (GTA) welding.[22–25] The smaller reaction area of the molten pool with monatomic nitrogen, which is confirmed by the monochromatic image of a specific spectrum line emitted by monatomic nitrogen,[23,25] is considered to lead to less nitrogen absorption during CO_2 laser welding than during arc welding. The difference in nitrogen absorption between CO_2 laser welding and YAG laser welding is attributed to the low level of monatomic nitrogen during YAG laser welding.

Though laser welding is expected to be effective in HNSs due to its small fusion zone and short thermal cycle, which may increase the solidification rate above the nucleation rate of bubbles, too little is known about the effect of laser welding on the nitrogen content in the HNS weld pool.

In order to control the amount of nitrogen exchanged with the atmosphere by the HNS weld metal, fundamental knowledge of nitrogen behavior during laser welding is necessary. The objective of the present study was to clarify the nitrogen behavior for HNS during laser welding.

II. EXPERIMENTAL PROCEDURE

The base material plates used in the present study were two kinds of HNS containing about 0.32 and 0.53 pct nitrogen, respectively. They were made by solid solution at 1273 K for 1 hour, and then cooled by water. The chemical compositions of both materials are given in Table I. Both had dimensions of $10 \times 50 \times 5$ mm. After their surfaces were cleaned and sanded to improve the absorptivity of the laser beam, the specimens were placed in a welding atmosphere-controlled chamber, the same as that used in a previous study,[24] as schematically shown in Figure 1. The power of the CO_2 laser was 5 kW. Shield gas with the same gas mixture as the atmosphere was provided coaxially with the laser beam at a flow rate of 4.2×10^{-4} m^3/s. The focus position of the laser beam was just on the top surface of the weld plates.

Bead-on-plate welding by the CO_2 laser at a travel speed within the range of 0.01 through 0.04 m/s was carried out

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Table I. Chemical Compositions of Materials Used in the Present Study (Weight Percent)

Material	C	Si	Mn	P	S	Ni	Cr	Mo	O	N
HNS (0.32 pct N)	0.01	0.2	1.5	0.022	0.002	9.0	22.0	—	0.011	0.3154
HNS (0.53 pct N)	0.02	0.2	5.9	—	—	10.1	23.1	2.0	0.016	0.5275

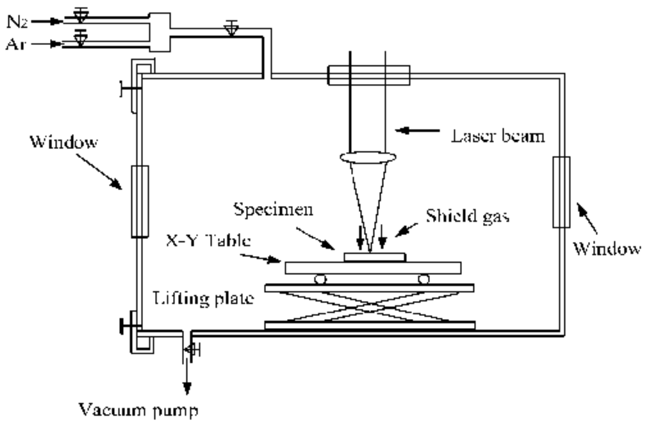

Fig. 1—Schematic illustration of the welding chamber controlling the CO_2 laser welding atmosphere.

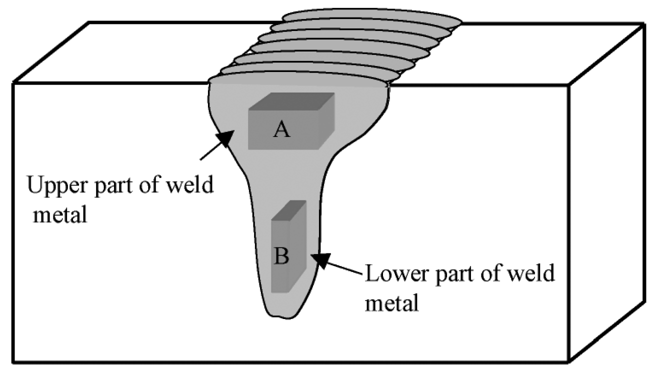

Fig. 2—Locations of samples in the CO_2 laser weld used for nitrogen analysis.

in the chamber, with nitrogen partial pressure varied from 0 to 0.1 MPa in an Ar-N_2 gas mixture and the total pressure (Ar + N_2) being maintained at 0.1 MPa. Since the nitrogen content of the weld metal is influenced by oxygen,[26–29] air was first eliminated from the welding atmosphere by evacuating the inside of the chamber to less than 10 Pa, after which the chamber was filled with the desired gas mixture.

Both ends of the cross section perpendicular to the weld were polished and etched to clarify the outline of the weld metal. The samples were carefully cut from the weld within the outline of the weld using an electrical-discharge machine. All surfaces of the block samples for nitrogen analysis were etched and observed to ensure that the samples consisted only of the fusion zone. The samples were then cleaned by filing away the surface and washed with acetone for 300 seconds by an ultrasonic cleaner. The nitrogen contents of samples were determined by fusion gas chromatographic analysis in an inert gas atmosphere by LECO* (a model TC-436DR oxygen and nitrogen analyzer). Reported data were the average of more than two values for one measurement, and data scatter was within the range of 50 ppm, which ensures a high reproducibility of the nitrogen contents.

*LECO is a trademark of LECO Corporation, St. Joseph, MI.

For comparison, nitrogen absorption during GTA welding was also conducted. To minimize the influence of the reaction surface of the molten weld on the nitrogen absorption as much as possible, the GTA welding condition was chosen so as to keep the bead width of the GTA weld as narrow as that of the CO_2 laser weld. The GTA welding was carried out in an Ar-N_2 mixture atmosphere of 0.1 MPa using the same materials as in the CO_2 laser experiment with the following welding parameters: a welding current of 150 A, an arc length of 1 mm, and a travel speed of 3.33 mm/s, which are different from the previous study.[22]

IV. RESULTS AND DISCUSSION

A. *Nitrogen Desorption during CO_2 Laser Welding*

As discussed in a previous article,[24] the surface of the molten pool can be reasonably divided into two parts according to the characteristics of laser welding: one in the upper part of the molten pool, which is in contact with the atmosphere of the CO_2 laser welding, and the other in the keyhole, which is in contact with the metal vapor. To investigate the nitrogen absorption and desorption during CO_2 laser welding, the molten pool can be divided into two parts, according to the cross-sectional shape of the weld metal during CO_2 laser welding. One is in the upper shallow region, and the other one is in the keyhole region, as shown in Figure 2. Position "A" corresponds to the samples used for nitrogen analysis in the upper part of the weld metals. Position "B" corresponds to samples used for nitrogen analysis in the keyhole in this experiment.

The experimental results on the nitrogen contents in both parts of the weld metals of two HNSs, containing 0.32 and 0.53 pct N, respectively, during CO_2 laser welding, are shown in Figures 3 and 4. The nitrogen contents in both parts of the weld metals of all the materials increase with the nitrogen partial pressure at low-nitrogen partial pressures and then tend to level out with further increases in the nitrogen partial pressure. No porosity is found in the weld metal under any nitrogen partial pressure, which is similar to the results for steels with low nitrogen content.[24] Contrary to the results of steels with low nitrogen contents,[24] the nitrogen content in the keyhole is somewhat higher than that in the upper part of HNS at all the nitrogen partial pressures, the same phenomenon as in the case of 329J1 stainless steel containing 0.15 pct nitrogen under a nitrogen-free (*i.e.*, pure argon) atmosphere.[24] Meanwhile, the nitrogen content in both parts of the weld metals of HNS is less than the as-received concentrations. This means that nitrogen desorption occurs at all nitrogen partial pressures and suggests that it is greater in the upper part of the molten pool.

Previous studies have suggested that the nitrogen partial pressure of the surface of a molten pool in contact with metal

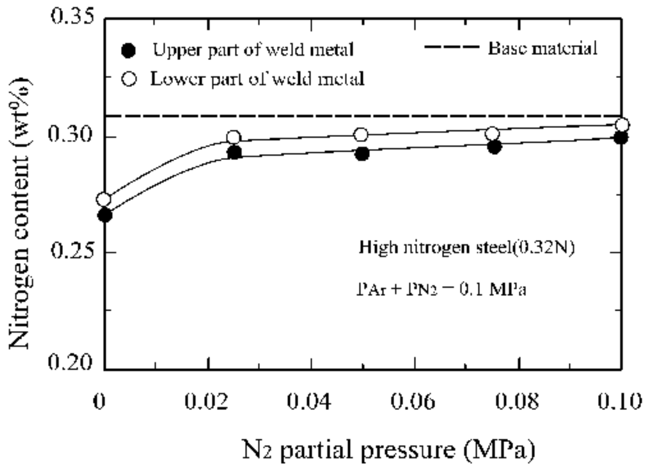

Fig. 3—Nitrogen contents in the upper part and lower part of CO_2 laser HNS (0.32 pct N) weld.

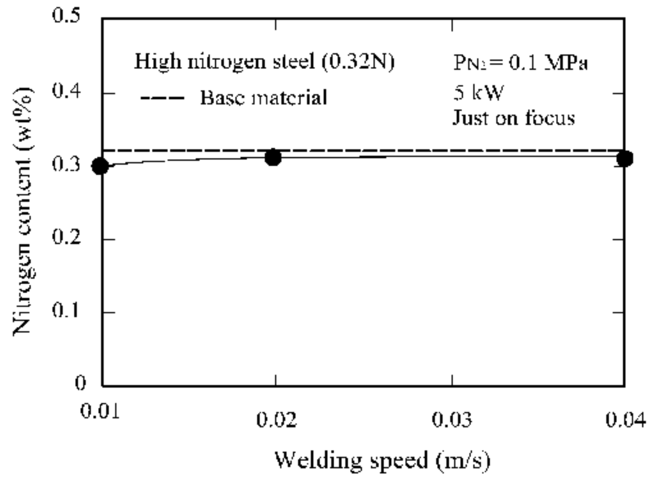

Fig. 5—Effect of traveling speed on the nitrogen content.

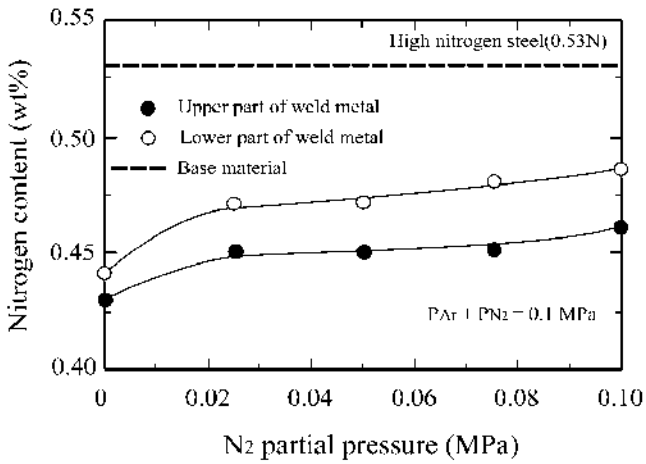

Fig. 4—Nitrogen contents in the upper part and lower part of CO_2 laser HNS (0.53 pct N) weld.

vapor in the keyhole can be decreased to a low degree due to the high pressure of metal vapor.[22,24] The higher nitrogen content in the keyhole region of the HNS weld metal implies that the existence of metal vapor, which covers the surface of molten metal, may not only limit the nitrogen absorption, but may also retard the nitrogen desorption from the molten HNS weld metal during laser welding.

Discussion in previous reports in the literature[24,25] suggests that the molten metal in the keyhole hardly absorbs and desorbs nitrogen because of the very high partial pressure of metal vapor in the keyhole, while the shallow molten metal (upper part) around the keyhole does desorb nitrogen. During movement of the laser, some portion of the upper shallow region containing less nitrogen due to desorption always fills the keyhole and mixes with the molten metal there, which contains a greater amount of nitrogen. However, the thermal cycle during laser welding is not long enough for sufficient stirring of the molten pool before solidification. In addition, the fact that the duration of the molten pool in the lower part is shorter than that of the upper part may also contribute to the lower nitrogen desorption from the molten pool in the keyhole region.

To investigate the effect of the duration of the molten pool on the nitrogen desorption in the weld metal, the relationship between the welding speed and the nitrogen content of the weld metal was examined using an HNS with 0.32 pct N during CO_2 laser welding under a nitrogen atmosphere. Experiments were carried out at a focus position on the HNS (0.32 pct N) plate surface ($F_d = 0$) in keyhole mode. The samples for the nitrogen analysis in this experiment all came from the upper part of the weld metals, as in a previous study.[24] The results are shown in Figure 5. For comparison, the nitrogen content of as-received HNS base material indicted by a dash line is also shown in this figure. The results show that the nitrogen content in laser-weld metal slightly increases with the welding speed. The longer duration of the molten pool of the weld metal results in the longer time available for nitrogen desorption from the HNS, to some extent. This may also partially support less nitrogen desorption in the lower part, as shown in Figures 3 and 4. As will be discussed in Section B, the as-received nitrogen content of HNS base materials is higher than the equilibrium nitrogen solubility calculated by Sieverts' Law at molten temperatures. The decrease in laser-welding speed leads to an increase in the nitrogen desorption time, which approaches to the equilibrium solubility. Thus, the nitrogen content of laser-weld HNS metal may be controlled mainly by nitrogen desorption.

Because the nitrogen solubility in liquid iron increases with a decrease in temperature under the same partial pressure of the monatomic nitrogen in the gas and because the temperature of the molten metal surface is thought to be lower in the upper part than in the keyhole as showed in previous studies,[11,13,14] the higher nitrogen content in the upper part of the laser-weld metal of steel with lower nitrogen content[23,24] can also be supported by the temperature dependence of the nitrogen solubility. However, this does not explain the behavior of HNS during laser welding, because the as-received nitrogen content is higher than the nitrogen solubility, which will be discussed in Section B.

Based on this discussion and considering that the volume ratio of the upper part to the lower part of the molten pool is large, nitrogen absorption and desorption in keyhole-mode laser welding are suggested to occur mainly in the upper part of the molten pool. The nitrogen content in the keyhole is always close to the as-received nitrogen content in the base material. This is similar to the case of steels with a low nitrogen content.[24]

B. *Comparison with Arc Welding and Equilibrium*

The equilibrium solubility of nitrogen in iron is given by Sieverts' Law, which states that the equilibrium nitrogen concentration in iron is proportional to the square root of the partial pressure of diatomic nitrogen gas. Since the surface of the molten pool in the upper part is in contact with the atmosphere of the CO_2 laser welding, and that in the keyhole is in contact with the metal vapor, the temperature of the laser-weld pool is assumed to be between the arc-weld pool temperature and the boiling point, which is thought to be around 3000 K for iron alloys. Based on the chemical compositions shown in Table I and the equations presented in previous article,[17,18] 1842 K is considered to be the temperature of molten metal of HNS (0.32 pct N) during GTA welding, and 1838 K is thought to be that of HNS (0.53 pct N), these two temperatures being 100 K over the melting point of these two kinds of HNS, respectively.

In consideration of this, the nitrogen content of the two HNS weld metals, that with 0.32 pct N and that with 0.53 pct N, during CO_2 laser welding with equilibrium nitrogen solubility, as calculated by Sieverts' Law at 1842 and 3000 K, respectively, are presented in Figures 6 and 7. Details of the method of calculation for the equilibrium nitrogen solubility can be found in a previous article.[24] The equilibrium nitrogen solubility at the temperature of the molten weld pool was calculated in an atmosphere of 0.1 MPa nitrogen. The square root of nitrogen partial pressure P_{N2} is adopted as the transverse axis in the figures. As suggested in Section A, as well as in a previous article,[24] the nitrogen absorption and desorption during CO_2 laser welding mainly occurs in the upper part of the molten surface, and thus the samples for nitrogen analysis in this experiment were all from the upper part of the weld metals.

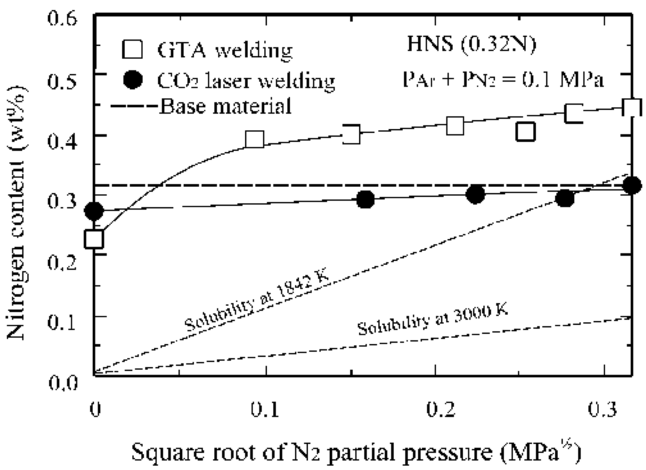

Fig. 6—Comparison of the nitrogen contents of HNS (0.32 pct N) during CO_2 laser welding, arc welding, and equilibrium solubility by Sieverts' Law.

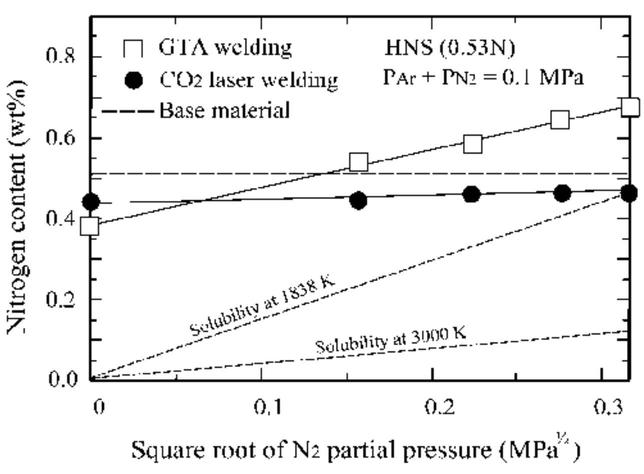

Fig. 7—Comparison of the nitrogen contents of HNS (0.53 pct N) during CO_2 laser welding, arc welding, and equilibrium solubility by Sieverts' Law.

Figure 6 shows that the as-received and weld metal nitrogen contents of HNS (0.32 pct N) during CO_2 laser welding are higher than the nitrogen solubility at the two temperatures, except when nitrogen partial pressure is around 0.1 MPa at the temperature of 1842 K. As for the result of HNS (0.53 pct N) shown in Figure 7, the as-received and weld metal nitrogen contents of HNS (0.53 pct N) during CO_2 laser welding are higher than the nitrogen solubility at the two temperatures within all the nitrogen partial pressures.

For comparison, the nitrogen contents in HNS (0.32 pct N) and HNS (0.53 pct N) weld metals during arc welding are also shown in Figures 6 and 7. The nitrogen content in HNS (0.32 pct N) weld metal during GTA welding increases with the nitrogen partial pressure. The nitrogen content in the HNS (0.32 pct N) weld metal during GTA welding is higher than the calculated nitrogen solubility at the two temperatures within all the nitrogen partial pressures. However, the nitrogen content in the weld metals of the two kinds of HNS during arc welding is lower than that during CO_2 laser welding under an argon atmosphere. This means that there is greater nitrogen desorption from the HNSs under an argon atmosphere during arc welding than during CO_2 laser welding.

Over a certain nitrogen partial pressure, the nitrogen content in the HNS (0.32 pct N) weld metal is higher than that in the base material and considerable porosity is observed in the arc weld metals when the nitrogen partial pressure is over 0.025 MPa, as shown in Figure 8. The tendency is the same as for HNS (0.53 pct N). However, compared with arc welding, no porosity has been found in CO_2 laser weld metals at any nitrogen partial pressures.

This result is considered to be the effect of the existence of monatomic nitrogen in the arc. As discussed in a previous article,[25] monatomic nitrogen exists much more widely over

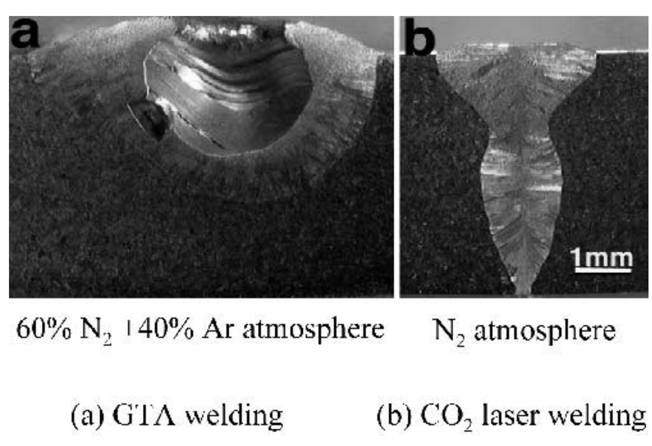

Fig. 8—Cross section of HNS (0.32 pct N) weld: (*a*) GTA welding under Ar-60 pct N_2 atmosphere and (*b*) CO_2 laser welding under nitrogen atmosphere.

the molten pool during arc welding than during CO_2 laser welding. Since there is a large quantity of monatomic nitrogen in the arc, the reaction of $N \rightarrow \underline{N}$ rather than that of $0.5N_2 \rightarrow \underline{N}$ is dominant in the nitrogen absorption of the GTA weld metal, which may result in the higher nitrogen content of the GTA weld metal than the nitrogen solubility calculated in an equilibrium state. The occurrence of considerable porosity in the GTA weld metal, as shown in Figure 8(a), can be reasonably considered in the following way. The excess nitrogen due to the reaction $N \rightarrow \underline{N}$ under the arc is ejected abruptly through the reaction $\underline{N} \rightarrow 0.5N_2$ into the non-arc atmosphere from the molten weld metal during cooling. However, one part of the excess nitrogen cannot be ejected from the molten weld metal because of the limited solidification period; then porosity forms.

On the other hand, as shown in Figures 3 and 4, the nitrogen content in the weld metal is less than the as-received content under any atmosphere during laser welding. Nitrogen absorption is controlled by the reaction of $0.5N_2 = \underline{N}$ on the top surface of the weld pool during laser welding because the amount of monatomic nitrogen in the atmosphere is much less than that during arc welding.[25] The keyhole during laser welding is formed by metal vapor when a high-density laser beam impinges on a small area of the sample. Because the pressure of the metal vapor in the keyhole is very high and the melting time is very short, both nitrogen absorption and desorption are considered to be quite small. Although the monatomic nitrogen is in contact with the molten pool, it is restricted to the area near the keyhole. The smaller reaction area of the molten pool with the monatomic nitrogen and the existence of metal vapor in the keyhole are considered to lead to less nitrogen absorption during CO_2 laser welding than during arc welding.[25] Thus, the increase of the nitrogen content in the laser-weld metal is less than that which occurs during arc welding. The reaction of $0.5N_2 = \underline{N}$ is promoted in the molten metal in the posterior part of the keyhole, because the molten metal is in direct contact with N_2. However, as for the reaction of $0.5N_2 = \underline{N}$, since the equilibrium nitrogen solubility is less than the nitrogen content of the base material, the desorption of nitrogen inevitably occurs. Although the nitrogen content is slightly increased with the increase of nitrogen partial pressure during laser welding, the nitrogen content is less than that in the base material, even in a nitrogen atmosphere. Compared with arc welding, the nitrogen absorption and desorption during laser welding are very small.

V. CONCLUSIONS

The nitrogen absorption and desorption by HNSs containing 0.32 and 0.53 pct nitrogen during CO_2 laser welding were investigated using an atmosphere-controlled chamber in which the nitrogen partial pressure was varied in an $Ar\text{-}N_2$ mixed gas atmosphere at a total pressure of 0.1 MPa. The following conclusions were reached.

1. The nitrogen content in the HNS weld metal during CO_2 laser welding was lower than that in the as-received base material in all conditions.
2. The nitrogen desorption was greater in the top part of the HNS weld metal than that in the keyhole region.
3. The nitrogen desorption in the Ar atmosphere was less during CO_2 laser welding than during arc welding.
4. With the increase in nitrogen partial pressure, the nitrogen content in the weld metal sharply increased during arc welding, but only slightly increased during CO_2 laser welding.
5. The nitrogen absorption and desorption of the HNS weld metal were much smaller during CO_2 laser welding than during arc welding.

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