Weldability of High Nitrogen Austenitic Stainless Steel Report 1

- Nitrogen Absorption of 316L Type Stainless Steel Welds in Extreme Environments -

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Abstract

Nitrogen absorption of 316L weld metal by high pressure GMA(constant arc length condition) process was investigated. The welding atmospheres were prepareted by pressurized N_2 and N_2-CO_2 gas mixture.. Also, the behavior of nitrogen in remelted weld metal containing high nitrogen and change of microstructure of welded were observed. The nitrogen content increased with increasing partial pressure of N_2. 0.60wt.% of nitrogen was absorbed in weld metal at 6.0MPA N_2 atmosphere. But this was very lower content than equilibrium solubility of 316L stainless steels at close to melting point. Nitrogen content in weld metal under pressurized N_2-CO_2 mixture atmosphere was different from pure N_2 atmosphere. The gas composition consists of PN_2-; 0.35MPA-P_{co2};0.05MPa(total pressure ;0.4MPa), it showed that maximum nitrogen content of 0.56wt.%.

KEY WORDS:(Nitrogen) (Absorption) (Stainless Steel) (Gas-Metal Reaction)

1.Introduction

The structural materials are demanded the properties of nonmagnetic, high resistance for corrosion , wear and high strength according to the development of the electronics, the precision and the cryogenic industry. Recently a new material of cold -rolled austenitics stainless steel which contained over 1% of nitrogen is candidate[1].

The characteristics for remelting and solidification of the new material aimed welding, however, dose not studied sufficiently yet.

The purpose of dioxide gas mixture atmospheric GMA method was discussed. The results of nitrogen content (n) were discussed referring to thermodynamical equilibrium date also.

2. Experimental Procedure

The chemical compositions of steel used was shown in **Table 1**.

The size of specimen is 12mm in thickness, 100mm in width and 200mm in length. The gas metal arc (GMA) process was used in high pressure atmosphere. The consumable electrode wire with 1.6mm diameter was used also.

Table 1 Chemical composition of base metal and electrode wire (mass%)

Material	C	Si	Mn	P	S	Cr	Ni	Mo	N	O
SUS316L	0.017	0.65	1.21	0.03	0.02	17.01	12.29	2.07	0.018	0.004
SUS316L,1.6mmφ	0.016	0.50	1.82	0.019	0.021	19.24	12.71	2.42	0.05	0.012

Figure 1 shows the stainless steel chamber with 1.8m³ volume capacity for the high pressure welding .

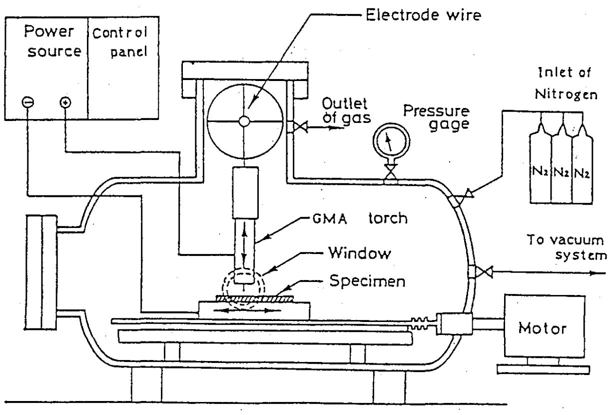

Fig. 1 Arrengement of equipment

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The atmospheric pressure in the chamber can be changed from about 15Pa to 6.5MPa. The head of an automaticMIG, TIG and Sub-marged arc welding machine are able to mount in this chamber.

Bead on plate welding performed by means of direct current power source which has an open circuit voltage of 80V (1000A).

The chamber was evacuated to a pressure until under 100Pa and then filled with the desired gas pressure and gas compositions.

Surface ground and cleaned test specimens were set in the chamber.

The distance between the contact tip and the specimen surface was 35mm. The welding current was about 200A. Travel speed of specimen was 3.3 mm/s. The visual arc length was approximately 10mm.

The nitrogen and oxygen content of deposited metals were analyzed by leco equipment.

Surface appearance was checked and microstructure of weld metal was observed by optical microscope or SEM. The lattice parameter measurement and Vicker's hardness test were applied to weld metals.

3. Experimental Results and Discussion

3.1 Nitrogen absorption under high pressure pure nitrogen

The surface appearances of weld metal obtained in various nitrogen pressure from 0.1MPa to 6MPa using GMA welding are shown in **Fig. 2**.

There is no defect on the bead surface as a blowholle or crack.

Its geometry seems smooth and without peculiar shape. Arc voltage is varied by pressure of atmosphere from about 68V at 0.1MPa to about 90V at 6.0MPa. Constant arc length condition by means of drooping characteristitic power source was used in this work.

So, the effect of pressure appears in the arc voltage change directly. Because , the density of nitrogen gas increases and cooling effect of the arc column increase also. The arc is constricted, consequently, arc voltage raises remarkably. The nitrogen content (N) of weld metal as a function of ambient nitrogen pressure are shown in **Fig. 3**. N increases with increasing of nitrogen pressure and N shows approximately 0.6 mass% at 6MPa. N content reported by T-Kuwana et.al [2] is plotted in the same figure (base metal 304 stainless steel). Comparing with T-Kuwana's result, the present result shows higher nitrogen content. This reason can predict as follow. Constant arc voltage control condition had been applied by T-Kuwana's work. In his code, it was observed that arc length decreased with increase of pressure. It means that reaction time

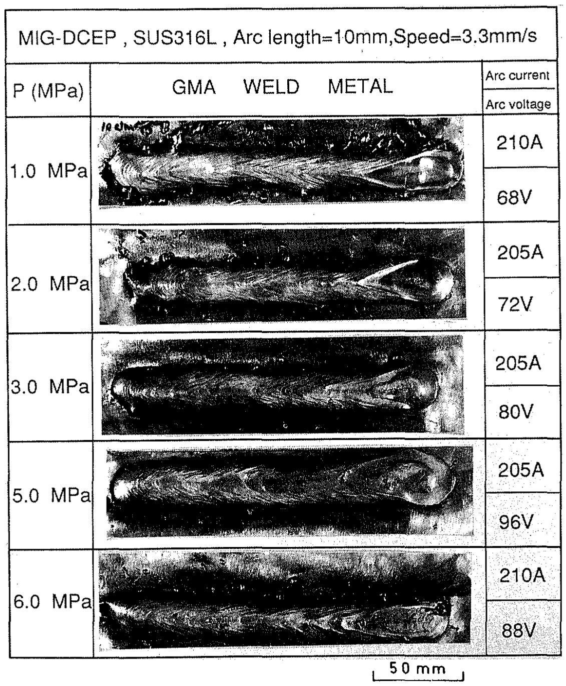

Fig. 2 Morphologies of bead appearance

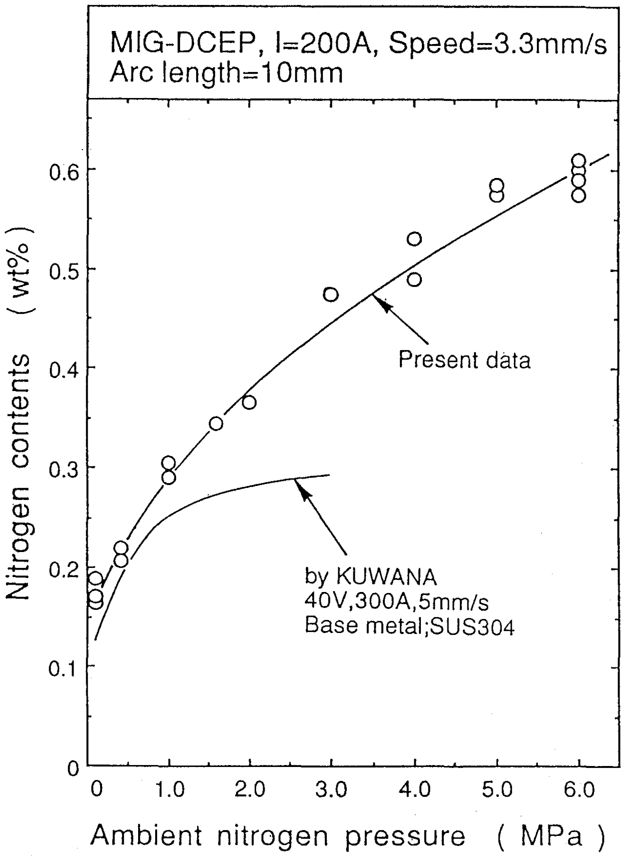

Fig. 3 Effect of ambient nitrogen pressure on nitrogen content

molten metal and nitrogen has becomes much shorter. But, in case of constant arc length condition like this work, nitrogen absorption was not hindered by the change of arc length resulting high pressure arc atmosphere.

Themodynamical discussion on the nitrogen absorption of the stainless steel weld metal in high pressure GMA process is considered as fellows.

Usually, an equilibrium state, the relationship between the nitrogen absorption in liquid iron or liquid stainless steel is described by the following equation.

$$\frac{1}{2} N_2 = N \text{ (in liquid iron)}$$

$$K = \frac{a_N}{\sqrt{P_{N_2}}} = \frac{[\%N\,(\text{iron})]}{\sqrt{P_{N_2}}} \cdots (1)$$

$$\log K = -\frac{188}{T} - 1.248$$

$$\frac{1}{2} N_2 = \underline{N} \text{ (in liquid stainless steel)}$$

$$K = \frac{a_N}{\sqrt{P_{N_2}}} = \frac{[\%\underline{N}\,(S.S)\cdot f_N^{(S.S)}]}{\sqrt{P_{N_2}}} \cdots (2)$$

Where K : the equilibrium constant

%N(S.S) : the solubility of nitrogen in liquid stainless steel%

$f_N^{(S.S)}$: the activity coefficient of nitrogen in liquid stainless steel

$(\approx f_N \cdot f_N^{(Cr)} \cdot f_N^{(Ni)} \cdot f_N^{(Si)} \cdot f_N^{(Mn)} \cdot \cdot \cdot)$

$f_N' \approx 1$

$f_N^{(M)}$: the effect of alloying element M on the activity coefficient of nitrogen

P_{N_2} : the nitrogen partial pressure (at)

a_N :activity of nitrogen

from equation (1) and (2) , equation (3) is given.

$$\%N_{(S.S)} = \frac{[\%N_{(iron)}]}{f_N^{(S.S)}} \cdots (3)$$

$f_N^{(S.S)}$ in equation (3) is expressed by Wagner's[3]equation as follows.

$$f_N^{(S.S)} = e_N^{(Cr)} \cdot [\%Cr] + e_N^{(Ni)} \cdot [\%Ni] + e_N^{(Mo)} \cdot [\%Mo] + e_N^{(Mn)} \cdot [\%Mn] \cdots (4)$$

where $e_N^{(M)}$ $(=\partial \log f_N^{(M)} / \partial \%M)$ is an interaction parameter.

It can be known that Cr, Ni, Mo and Mn content of weld metal by chemical analysis. $f_N^{M'}$(activity coefficient) is determined from the figure in an equilibrium study by Humbert [4] and works of Phelke and et.al [5] so, $f_N^{(s.s)}$ is given as follows.

$f_N^{(s.s)}$1873K=0.181

An equilibrium solibility of 316L stainless steel at 1873K is given in equation(5)

$$\%N_{(S.S)},1873 = 5.52\,K \cdot \sqrt{P_{N_2}} \cdots (5)$$

The equation (5) means that the equilibrium solibility of nitrogen in the liquid stainless weld metal is 5.52 times that in pure iron weld metal.

But, nitrogen content of 316L stainless steel weld metal in the result, is much lower content.

This experimental result means that in GMA welding, reaction time between molten weld metal and nitrogen gas is much shorter than that of equlilbrium solibility measurements.

On the other hand, it has been reported that the solibility of nitrogen molten stainless steel decrease with increasing of temperature.

Using Nelson's equation [6], solilitity of nitrogen as function of temperatures is calculated as follows. Relation between the activity coefficient of nitrogen and temperature is described by the following equation (6).

$$\log f_N^{(S.S)} = \frac{1873}{T} [\Sigma \log f_N^{(M\,1873)}] \cdots (6)$$

From equation (5) and (6), equation (7) is given.

$$[\%N_{(S.S)}] = \frac{K}{f_{N\,1873}^{\,SS\frac{1873}{T}}} \cdot \sqrt{P_{N_2}} \cdots (7)$$

where $\log K = -\frac{188}{T} - 1.248$

f N 1873K=0.181

Using equation (7), solibilities of nitrogen from 1873K to 2273K were calculated. Obtained nitrogen content as a function of the square root of nitrogen pressure are shown in **Fig. 4**.

Results of this work are shown by open circles in the same figure. Nitrogen cintent obtained by this experiment, can not attain the equibirium solibility at higher pressure because of shortage of reaction time. At $\sqrt{PN_2}$ above 1MPA, liner relationship is observed between nitrogen content of weld metal and nitrogen pressure.

Appearently K calculated is 0.268. Relation between weld metal nitrogen contents and base metal

nitrogen contents are shown in **Fig. 5**.
Nitrogen pressure of GMA welding were changed from 0.1MPa to 6.0 MPa. From Fig. 5, it can be estimated that minimum nitrogen pressure for GMA required by base metal nitrogen content.

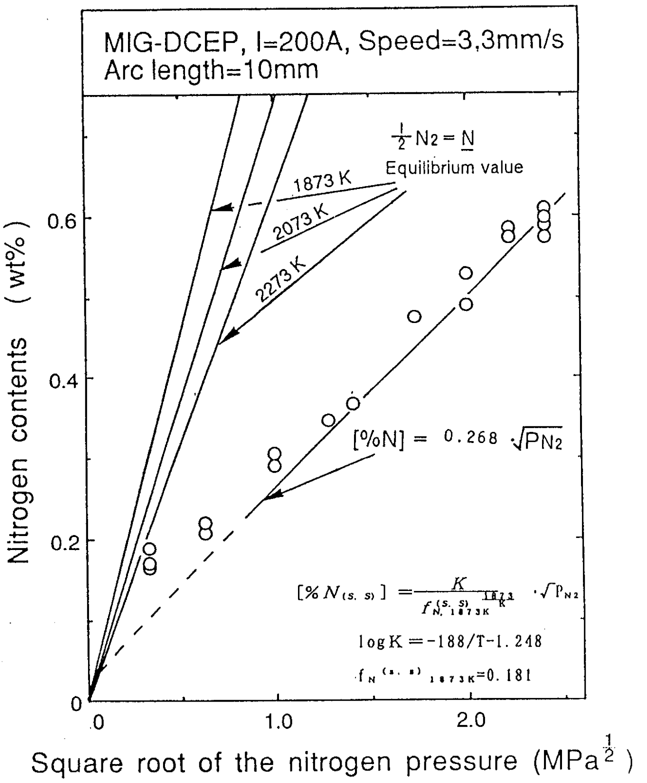

Fig. 4 Relationship between square root of the nitrogen pressure and nitrogen contents

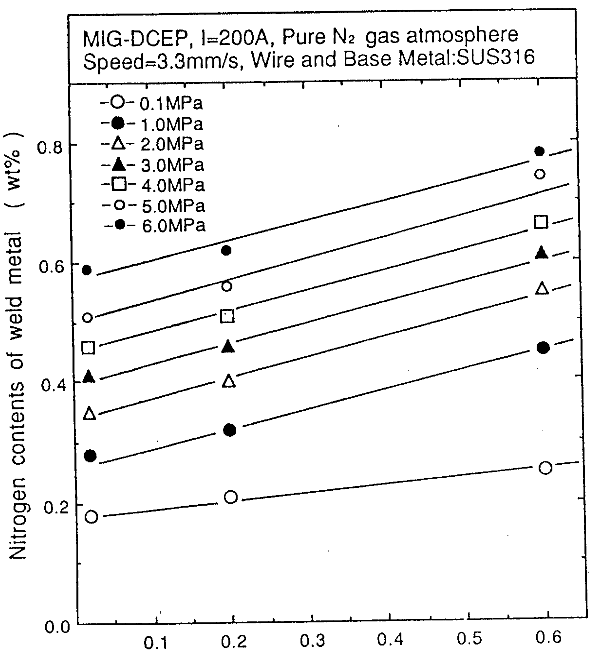

Fig. 5 Relationship between nitrogen contents of weld and base nitrogen content

Also, about 0.8 % nitrogen weld metal is given by 6MPa nitrogen pressure. In the weld metal, no micro void or crack were observed.

3.2 Nitrogen absorption under high pressure nitrogen -carbon dioxide gas mixture.

It was reported [7)] that nitrogen absorption of weld metal is accelerated by presence of carbon dioxide gas in nitrogen shielding gas on GMA process. So, in order to higher nitrogen contained stainless steel weld metal, GMA welding was carried out in pressurized N_2-CO_2 gas mixture.

Figure 6 shows the relationship between nitrogen contents of weld metal and CO_2 % in welding atmosphere. Welding was carried out in from 0.4 MPa to 6 MPA xmi tured gas.

An acceleration of the nitrogen absorption of weld metal by presence of CO_2 shows at 0.4MPa N_2-CO_2 gas mixture.

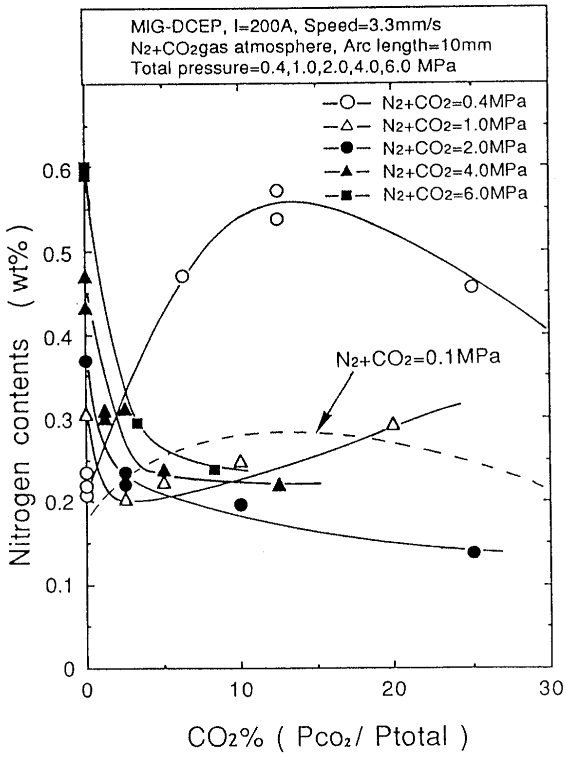

Fig. 6 Effect of CO% on the nitrogen contents of weld metal

But, at above 2MPa, addition of CO_2 into arc atmosphere is of no effect. But, at above 2 MPa, addition of CO_2 into arc atmosphere is of no effect. Weld metal surface was covered by oxide film and bead wide slightly increased by CO_2 addition.

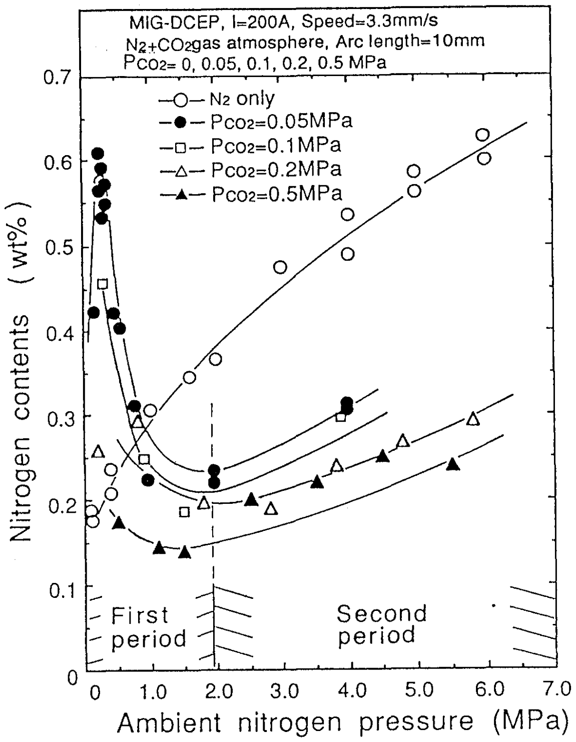

Fig. 7 Effect of nitrogen pressure in N2-CO2 mixture on the nitrogen contents of weld metal

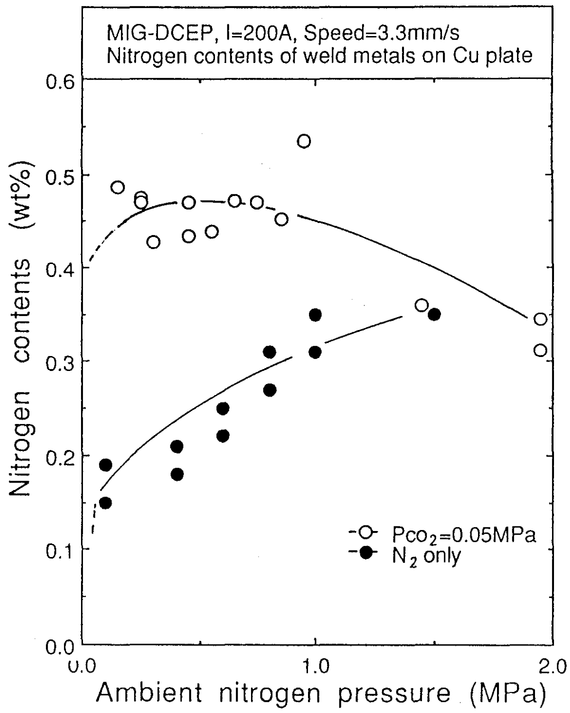

Fig. 8 Relationship between nitrogen contents of transferred droplets and the nitrogen pressure

Relation between nitrogen contents and nitrogen pressure of N_2- CO_2 mixture atmosphere is shown in **Figure 7**. Partial pressure of CO_2 is marked in the same figure. An accelerative effects of the nitrogen absorption by CO_2 presence are observed at less than about 1MPa nitrogen and less than 0.1MPa CO_2 (1st period). Ambient nitrogen pressure not be less than 2MPa, an accelerative effect has not been observed. (2nd period).

Welding was carried out on the water cooled Copper plate. By this method, droplets which reacted to arc atmosphere could be collected.

Relation between nitrogen contents droplets and nitrogen pressure is shown in **Figure 8**. Open circle means in N_2-CO_2 gas mixture and closed circle is pure N_2 respectively. In N_2-CO_2 gas mixture, the droplets absorbed a lot of nitrogen from atmosphere during the transfer process in the arc.

It was stimulated by CO_2 coexisting N_2. It is commonly produced in the arc by the dissociation of CO_2 into carbon monoxide and oxygen in the arc. Oxygen has strong effect on molten metal.

It is known that oxide film formed on the molten droplet surface retards nitrogen desorption. Also, the effect of NOx produced in arc atmosphere estimated [7]. Surface activation effect of oxygen is important.

2nd period in Fig. 7, nitrogen contents of weld metal in high pressure N_2-CO_2 atmosphere are lower than that of pure N_2 atmosphere.

It is considered that nitrogen absorption into weld metal retards in this atmosphere rather than acceleration by CO_2.

Weld metal oxygen content was analyzed. It was approximately 0.06-0.08%. As stated above, oxygen in the molten metal disturbs strongly the adsorption and desorption rate of nitrogen. In this case, it is estimated that nitrogen absorption from weld pool retards by formed oxide film on the surface.

The effect of oxygen content on the nitrogen contents of weld metal was examined. Different oxygen content base metals were used.

Relation between nitrogen contents of weld metal and nitrogen pressure is shown in **Fig. 9**. It is clear that high oxygen base metal (0.07wt%) shows lower nitrogen contents. So, nitrogen absorption from weld pool surface is depressed by covered oxide film on weld pool.

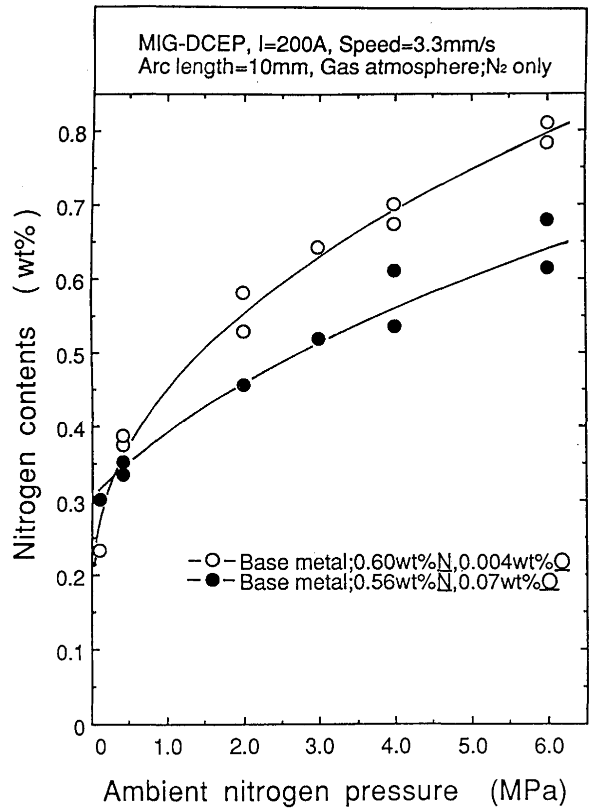

Fig. 9 Effect of oxygen content of base metal on the nitogen contents of weld metal

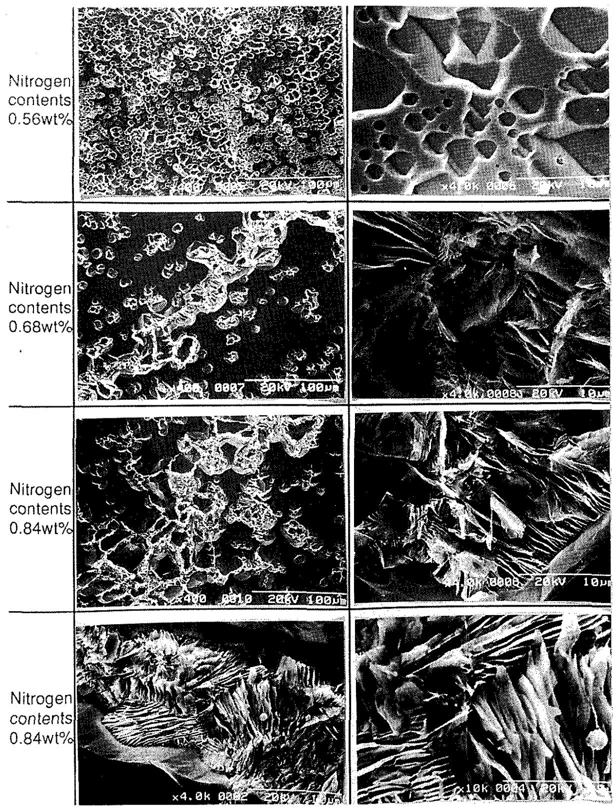

Fig. 11 Scanning electron micrographs of austenite and nitride in weld metal

3.3 Properties of high nitrogen weld metal

Figure 10 and **11** indicate the microstructures of weld metal.

Weld metals considered from an austenite single phase. Nitrides are observed in 0.68 and 0.84% nitrogen contained weld metal. As shown in Fig. 11, flake like nitrides are estimated as a Cr_2N [8]. The hardness of weld metal were measured by Vicker's hardness tester with the load of 200g*f*. As shown in **Figure 12**, the hardness increased with increasing of nitrogen content. For example, weldmetal contained about 0.6% nitrogen indicates beyond 250. Since the hardening behavior seems to relate solid solution hardening by nitrogen. So, the variation of lattice parameter were measured by X-ray diffraction method as shown **Figure 13**. The latlicee parameter increases with increasing of nitrogen contents. Solved nitrogen makes strain in austenite.

The increase of nitrogen content is well correspond to the change of lattice parameter. Therefore, it is condiered that most of nitrogen exists as solid solution

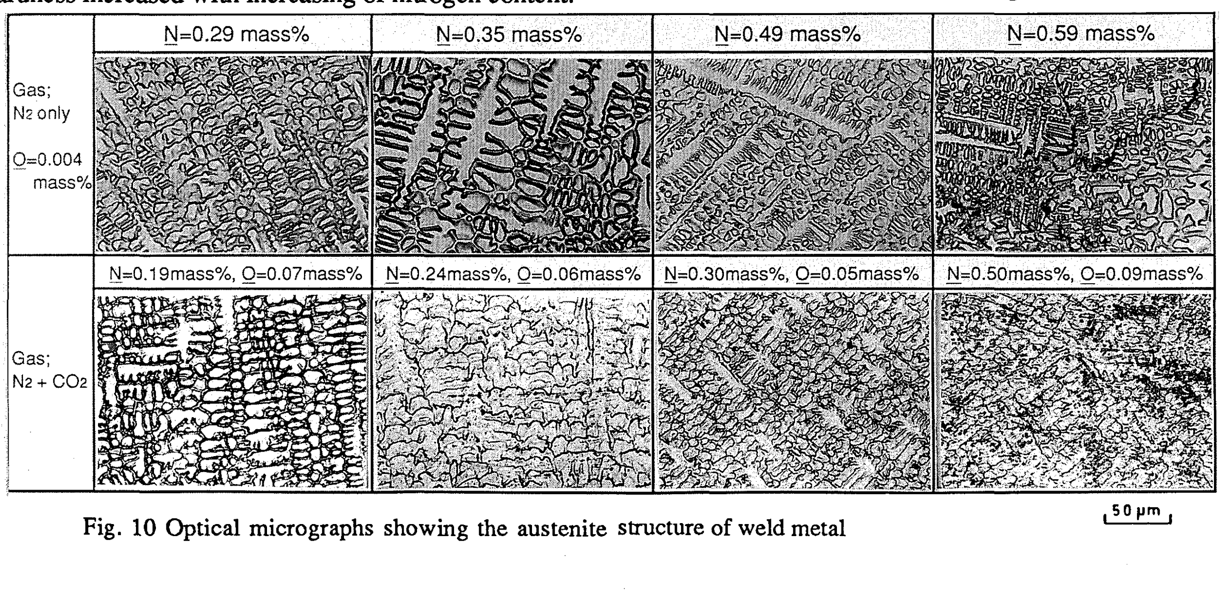

Fig. 10 Optical micrographs showing the austenite structure of weld metal

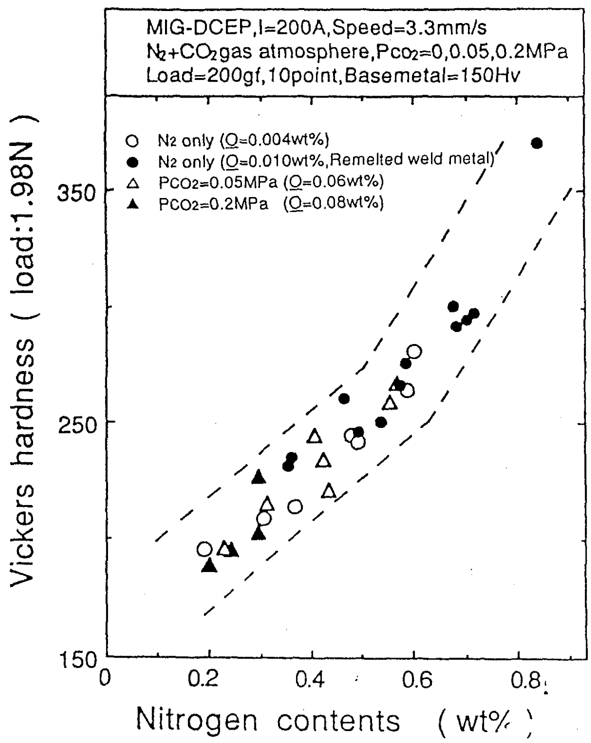

Fig 12. Effect of nitrogen content on vickers hardness of weld metal

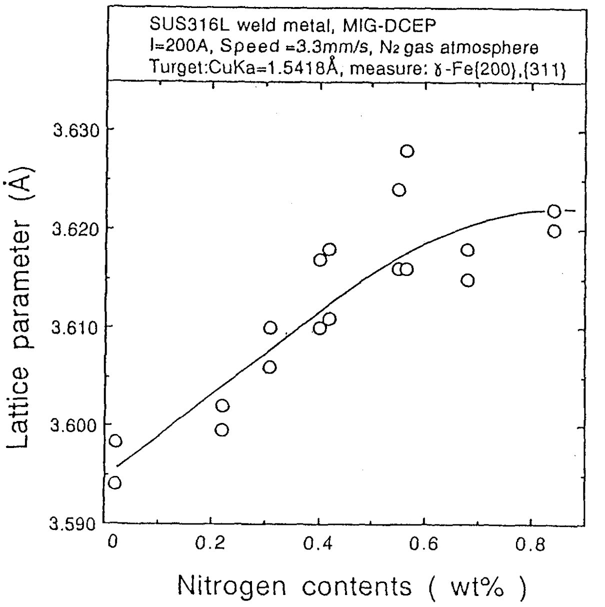

Fig. 13 Effect of nitrogen content on the lattice parameter of weld metal

in weld metal. Hardening behavior resulted by interstitial type nitrogen . But , in case of beyond about 0.7% nitrogen, it is estimated that the possibility of precipitation hardening by Cr_2N

4. Conclusions

Nitrogen absorption of 316L weld metal by high pressure GMA(constant arc length condition) process was investigated. The welding atmosphere was prepared by pressurized N_2 and N_2 and N_2-CO_2 gas mixture.

Bead on plate welding was carried out in pressurized N_2 and N_2-CO_2 atmosphere of 0.1 MPa-6.0MPa.

The results are summarized as follows.

(1) 0.6wt% of nitrogen was absorbed in weld metal at 6.0MPa pure N_2 welding atmosphere.

(2) Nitrogen content of weld metal is very lower content than equilibrium solibiity of 316L stainless steel at close to melting point.

(3) Nitrogen content in weld metal under pressurized N_2-CO_2 mixture atmosphere is different from pure N_2 atmosphere.

(4) The gas composition consist of PN_2=0.35MPa-PCO_2=0.05MPA (total pressure=0.4MPa), it shows that maximum nitrogen content of 0.56wt%

(5) Over 2MPa addition of CO_2, decreased nitrogen content of weld metal.

(6) About 0.84 wt% nitrogen content was obtained by remelting process under high pressure.

(7) The lattice parameter and Vicker's hardness number were increased linearly with increasing of nitrogen content.

(8) The nitrides were observed over 0.65wt% nitrogen weld metals.

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