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Influence of Nitrogen on the Structure and Low Temperature Impact Properties of 304 Type Austenitic Stainless Steel Weld Metals by SMAW Process†

T. ENJO* Y. KIKUCHI** and H. MOROI***

Abstract

Experimental covered electrodes (lime-titania type) were made by selective additions of Mn-nitride or Cr-nitride to the electrode covering. 304LN stainless steel base plates (t = 12 mm) whose edge preparation was machined to single sided V, 60° included angle were clamped in a jig and were welded together by multi-pass shielded metal arc welding process.

Nitrogen content of weld metals was adjusted by changing the content of Mn-nitride or Cr-nitride in the electrode covering.

Effect of nitrogen on the microstructure of weld metal, δ-ferrite content, mean grain width, hardness and δ-ferrite secondary arm spacing were studied. Impact test for as welded specimen and solution treated specimen have been carried out at temperature range from 77K to room temperature.

Influence of nitrogen on the impact value of weld metals was mainly discussed.

Results obtained are summarized as follows:

(1) δ-ferrite content in the weld metals in influenced largely by the nitrogen content.

(2) Impact value of weld metals increases with increasing of the nitrogen content of the weld metals up to about 1700 ~ 1800 ppm after then the impact value falls as the nitrogen further increased.

(3) The strengthening mechanism of weld metals due to addition of nitrogen is estimated that the effect of austenitic structure stabilized and interstitial solution hardening. Micro fissuring and precipitation of cluster (nitride) in excess of nitrogen containing weld metals decrease the impact value of weld metals.

(4) Nitrogen content up to about 1700 ~ 1800 ppm of weld metal which is introduced by SMAW process gives a good influence on the impact properties at low test temperature under condition of this study.

KEY WORDS: (SUS 304 Steel) (Weld Metal) (Nitrogen) (Impact Value)

1. Introduction

Low carbon austenitic stainless steel has a good mechanical properties at low temperature and extensive use of low temperature survice in industry. But it is well known that, the decreasing carbon content introduce to loss of strength, proof stress of austenitic stainless steel. The interstitial solution strengthening and the effect of stabilizing for austenite phase due to alloying of nitrogen are expected[1−2].

The influence of nitrogen on the welds or welding process does not make clear yet.

The effect of nitrogen and oxygen content on the low temperature impact properties of 304 type weld metals made by MIG process were already studied by authors and the results were reported in previous papers[3−4].

This study has been made to determine the influence of nitrogen on the structure and impact properties of weld metal made by shielded metal arc welding process (SMAW).

The covered electrodes (lime-titania type) were used in this study. It was changed that the content of Mn-nitride or Cr-nitride of the electrode covering. The weld metals which are different content of nitrogen are made by SMAW process using the experimental covered electrodes.

Relation between microstructure, low temperature impact properties of weld metal and nitrogen content of weld metals are investigated.

2. Experimental Methods

Shielded metal arc welding has been carried out automatically using A.C arc welding machine. The 7 kinds of the stainless steel SMA electrodes (lime-titania type) contained varying amounts of Mn-nitride or Cr-nitride in the covering were provided. And the austenitic stainless steel core wire in these electrodes were 4 mmφ and D308 grade.

Dimension of 304LN stainless steel used for base metals were t = 12 mm, 200 × 100 mm and surfaces of these specimens were deoxidized and degreased just before the welding.

† Received on May 1, 1986.

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Base metals with groove angle 60° in single side were clamped on a jig in the state of root gap 2 mm and then were welded together automatically by multi-pass (3 passes) SMAW process. Welding variables used are: arc voltage 28V, welding current 170A, welding speed 2.5 mm/sec. and electrodes were dried at 473K, 7.2ks. Nitrogen contents of weld metal were varied from about 630 PPM to about 2880 PPM but the contents of other main elements such as C, Mn, Ni and Cr were not changed.

The analysis of nitrogen was made by LEGO analyzer. Delta ferrite was examined by X-ray diffraction analysis and its content was determined by ferrite-scope. In this work, sub-size (10 X 7.5 X 55 mm) charpy V-notch specimens conforming to JIS Z3112 were extracted from the welded plates. The 2 mm -V notch was located in center part of weld metal perpendicular to the welding direction.

The impact test has been carried out at the temperature range from 77K to 273K. The chemical composition of flux used and an example of weld metal analyzed are shown in **Table** 1 and **Table** 2 respectively.

3. Experimental Results and Discussions

3.1 Structure of weld metal

The effect of nitrogen on the structure of weld metals were investigated. Columnar grains of the cross section of weld metal was observed. The columnar grains grow up from fusion boundary to the weld center line, along the steepest temperature gradients of the weld metal.

The mean widthes of columnar grains were determined by means of several times measurements on the weld. Relation between mean width of columnar grain and nitrogen content of weld metals($\underline{N}$) is shown in **Figure** 1. It seems that mean width of columnar grains of weld metals are not so hardly influenced by nitrogen content($\underline{N}$).

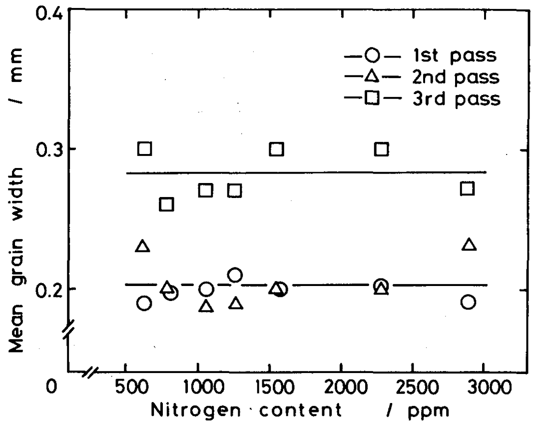

Fig. 1 Change in the mean width of columnar grains in weld metal with nitrogen content.

Table 1 Chemical composition of fluxes used.

(wt%)

Element \ Electrode	N 0	N 5	N 10	N 15	N 20	N 25	N 30
TiO_2	43.3	43.2	42.8	42.3	41.4	39.3	38.2
$CaCO_3$	21.2	21.2	21.2	21.2	21.2	20.2	20.2
SiO_2	10.2	10.2	10.2	10.2	10.2	10.2	10.2
CaF_2	6.4	6.4	6.4	6.4	6.4	6.9	6.9
Al_2O_3	1.8	1.8	1.8	1.8	1.8	1.8	1.8
K_2O	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Na_2O	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Fe-Cr	6.0	6.0	6.0	6.0	6.0	3.0	1.4
Cr_2N	0	0	0	0	0	5.5	8.3
Mn	5.5	5.1	3.7	1.8	0	0	0
MnN	0	0.5	2.3	4.6	7.4	7.4	7.4
Others	2.7	2.7	2.7	2.8	2.7	2.8	2.7

Table 2 An example of weld metal analyzed.

(wt %)

Electrode \ Element	C	Si	Mn	P	S	Ni	Cr	Ti	N
N 0	0.031	0.42	1.49	0.027	0.006	9.97	19.67	0.010	0.063
N 5	0.030	0.50	1.58	0.026	0.006	9.91	19.44	0.012	0.079
N 10	0.026	0.54	1.54	0.027	0.006	10.23	19.47	0.010	0.107
N 15	0.028	0.53	1.63	0.026	0.005	10.11	19.55	0.013	0.127
N 20	0.032	0.49	1.88	0.027	0.006	9.86	20.02	0.014	0.155
N 25	0.029	0.55	1.86	0.027	0.005	9.96	19.93	0.019	0.229
N 30	0.028	0.55	1.85	0.027	0.005	9.94	19.71	0.017	0.288

The mean width were approximately 0.2 mm on the 1st and 2nd pass, and was approximately 0.28 mm at 3rd pass. Namely mean width of columnar grain on the final pass became slightly the wider than that of 1st and 2nd pass. It is estimated that this result is occurred due to the difference of cooling rate and the disappearance of columnar structure or refinement of microstructure by reheating in subsequent weld passes[5].

Generally, weld metals made by SMAW process using D308L covered electrode, contain several % δ-ferrite. In this study, it seems that δ-ferrite content is changed by nitrides which are added to the electrode covering.

Relation between δ-ferrite content and $\underline{N}$ content is shown in **Figure** 2. It is observed that a significant decrease in δ-ferrite content with an increase in weld metal nitrogen. The weld metal become δ-ferrite free structure in case of $\underline{N}$ content is more than approximately 2,000 PPM. This result is same to that of previous paper[3].

Delta-ferrite morphology is varied from vermicular type to globular type[6] with a decrease in weld metal δ-ferrite content.

The secondary dendrite arm spacings of vermicular δ-ferrite were measured. That spacings were approximately 13 μm and 10 μm on the root pass (1st pass) and 3rd pass respectively.

It seems that the secondary dendrite arm spacings of vermicular δ-ferrite are not so hardly influenced by nitrogen content($\underline{N}$)(up to approximately 1100PPM). The effect of $\underline{N}$ content on the hardness of weld metals is shown in **Figure** 3. The hardness of weld metals slightly increase with increasing of nitrogen content.

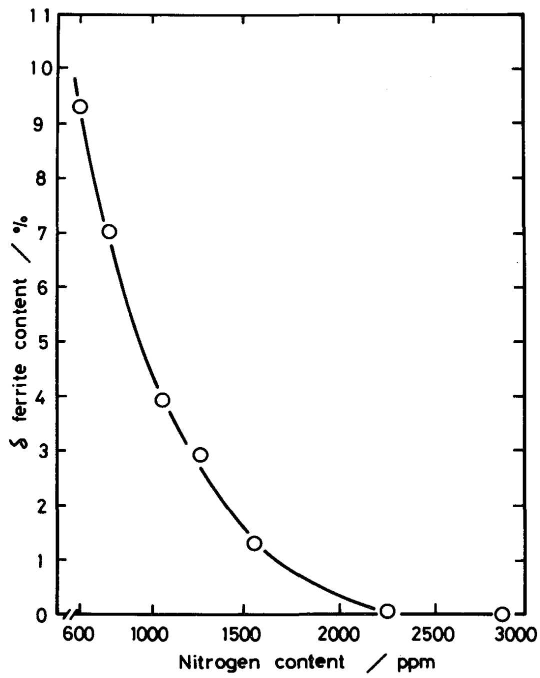

Fig. 2 Change in the δ-ferrite content of the weld metal with nitrogen content.

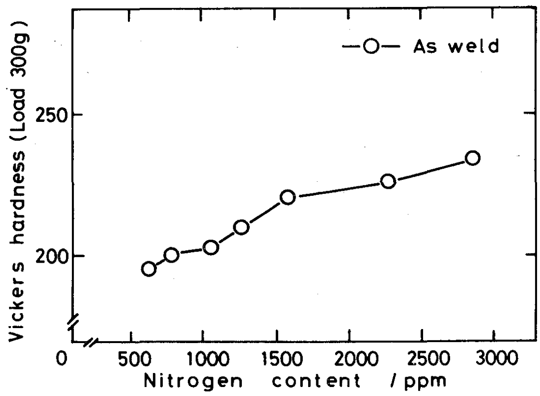

Fig. 3 Change in the hardness of the weld metal with nitrogen content.

And then, nitrogen has a significant effect chiefly on the δ-ferrite content of weld metal.

3.2 Low temperature impact properties of nitrogen contained weld metals

The impact test specimens were cooled in vacuum bottle up to the test temperature then were tested after holding for 30 min. at the test temperature. The results of impact test on the weld metals at various temperature are shown in **Figure** 4. The impact value of weld metals increases with increasing of $\underline{N}$ content up to approximately 1700 ~ 1800 PPM and after then falls as the nitrogen content further increase, that is very interesting behaviour. This general treands are observed at each testing temperature.

Relation between δ-ferrite content of weld metals and

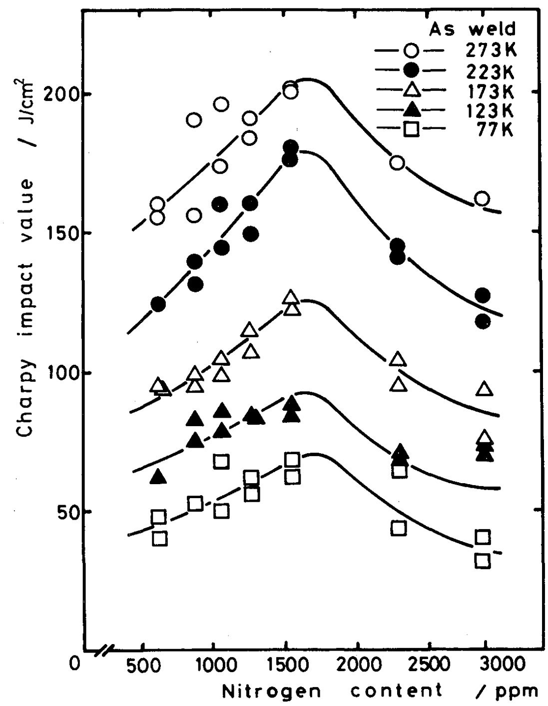

Fig. 4 Effect of nitrogen content on the charpy impact value of the weld metal at the low test temperatures.

charpy impact value is shown in **Figure** 5. It seems that charpy impact value decrease slightly with increasing of δ-ferrite content of weld metals, but N content of impact specimens are not same amount in this figure.

It may not be concluded from the δ-ferrit content that the decreasing of charpy impact value in Fig. 5. These results will be discussed in the later.

It is well known that strain-induced martensitic structure is formed when 304 type austenitic steel is deformed at low temperature.

The ferrite contents of specimens were measured before and after testing and the former and the latter is indicated B% and A% ferrite content respectively. Thus, apparent degree of martensitic transformation ($\alpha'\%$ = A% – B%) of ruptured specimens was determined.

It was known that values of α' were increases with decreasing of N content and decreasing of test temperature. Relation between α' content and charpy impact value is shown in **Figure** 6.

It seems that at 123K and 77K, charpy impact value are not changed by α' content but at 273K, 223K and 173K, decrease slightly with increasing with α' content. Next, the effect of α' on the hardness of weld metals is shown in **Figure** 7. The weld metals become slightly soft increasing with α' content is observed. Consequently in this study, it is cleared that charpy impact value are not influenced hardly by strain-induced martensitic transformation.

Figure 8 shows the fracture morphology for the specimens ruptured at 77K by using SEM.

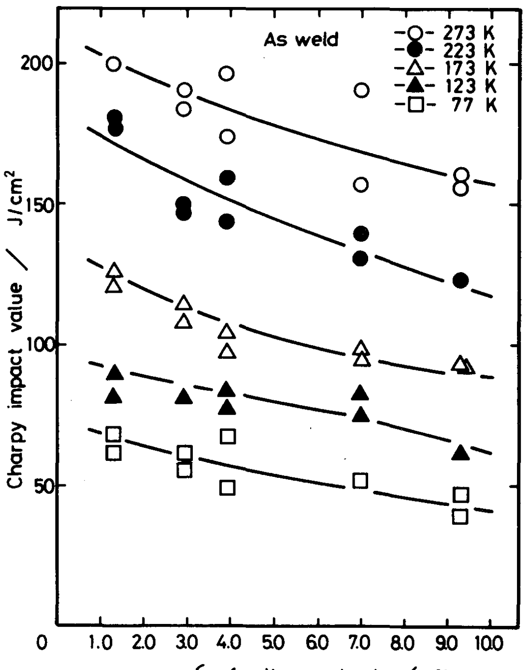

Fig. 5 Effect of δ-ferrite content on the charpy impact value of the weld metal at the low test temperatures.

Nitrogen contents are approximately 167 ~ 1546 PPM and in this range, charpy impact values increased with increasing with N content.

Photographs indicate the change in fracture morphology as a function of N content.

It is observed that the fracture mode become ductile fracture contained the many dimples with increasing of N content.

On the other hand, the impact value falls as the nitrogen further increased, and the fracture morphology is shown in **Figure** 9. Transgranular ductile fracture mode (a) or (b) and intergranular brittle fracture mode (a′) or (b′) are observed.

It is known that the presence of precipitations and segregated impurities at grain boundaries cause a intergranular brittle fracture[7] and the authors estimate that

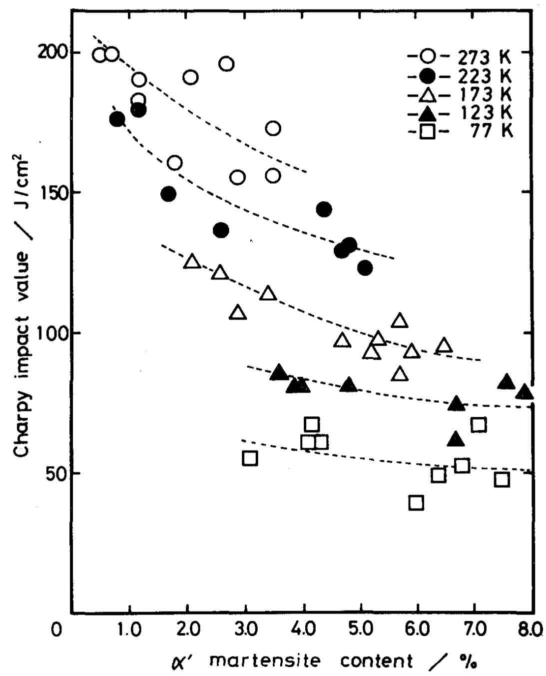

Fig. 6 Effect of α′-martensite content on the charpy impact value of the weld metal at the low test temperatures.

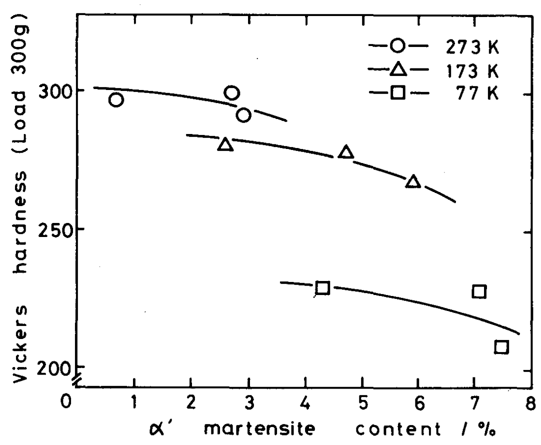

Fig. 7 Change in the hardness of the weld metal with α′-martensite content.

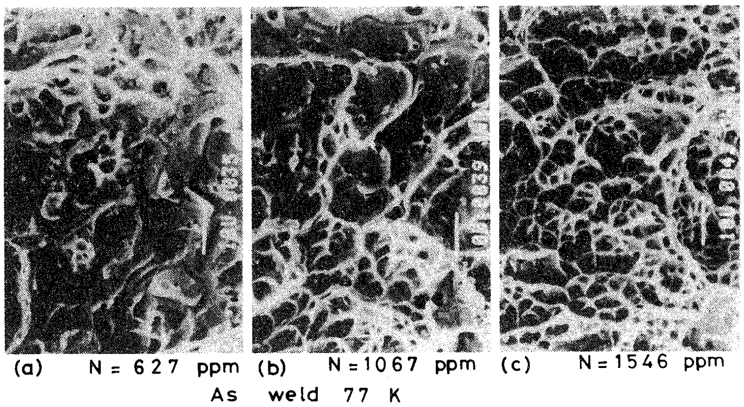

Fig. 8 Change in the fracture morphology of weld metal tested at 77K with nitrogen content. (N<2000 ppm)

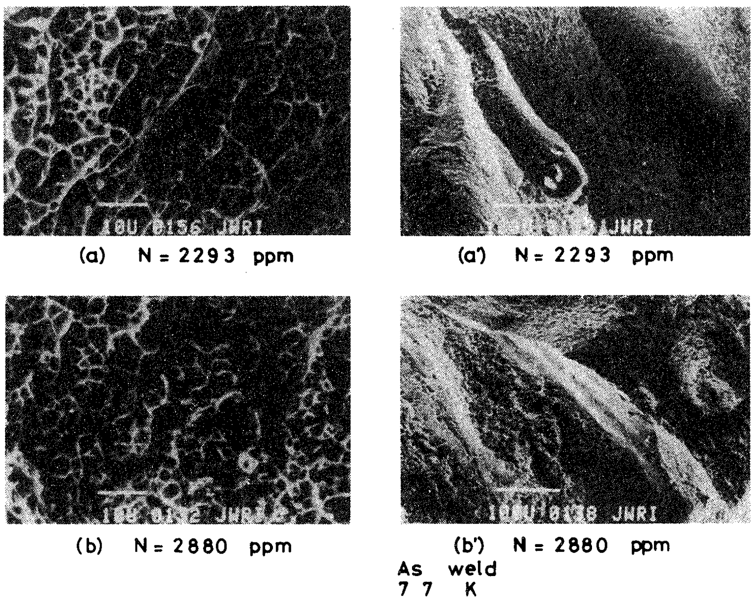

Fig. 9 Change in the fracture morphology of weld metal tested at 77K with nitrogen content. (N>2000 ppm)

the excess of nitrogen containing of weld metals decrease the impact value of them.

To clear that the effect of nitrogen content on the low temperature impact properties, the authors have to discuss the following items.

1) The effect of δ-ferrite of weld metals on the impact value.
2) The impact value increases with a function of nitrogen content up to the certain amount of weld metals after then the impact value falls as the nitrogen further increased.

Solution heat treatment[8] is carried out on the weld metals to control the δ-ferrite content. The following heat treatment conditions are used; Temperature 1323K, holding time 1.8 ks and then water quenching. The effect of solution heat treatment on the grain width of weld metals by measuring before and after solution heat treatment. And then it was clear that mean grain widthes were not influenced by heat treatment as shown in **Figure** 10. But the morphology of δ-ferrite was changed by heat treatment from vermicular type to globular type. Relation between $\underline{N}$ content of weld metals and δ-ferrite content of solution heat treated weld metals is shown in **Figure** 11. Delta-ferrite content is decreased by solution heat treatment.

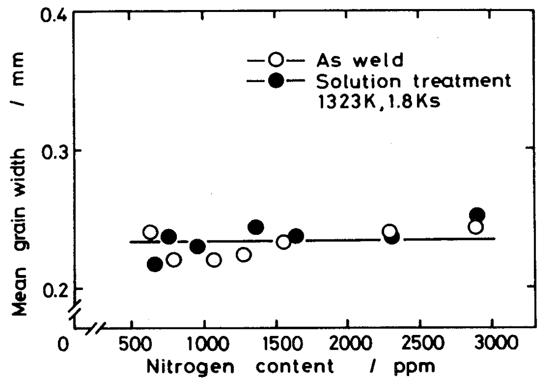

Fig. 10 Change in the mean width of columnar grains in solution treated weld metal with nitrogen.

The maximum δ-ferrite content is approximately 1.6% with $\underline{N}$ content from approximately 600 PPM to 1700 PPM. According to measurements of impact value of these weld metals, the results obtained at (a) 273K,

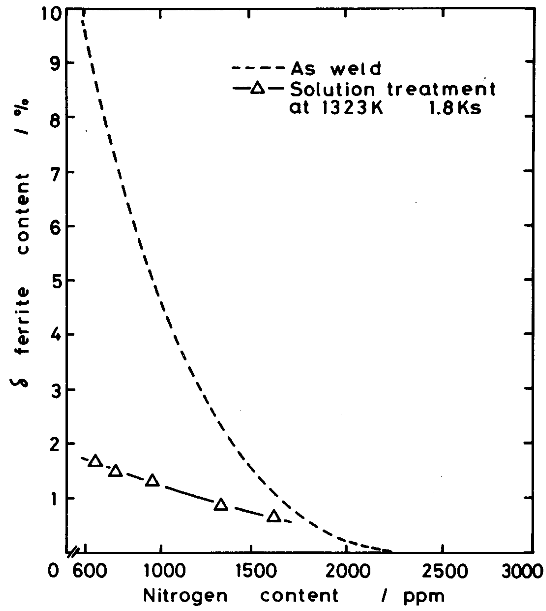

Fig. 11 Change in the δ-ferrite content of the solution treated weld metal with nitrogen content.

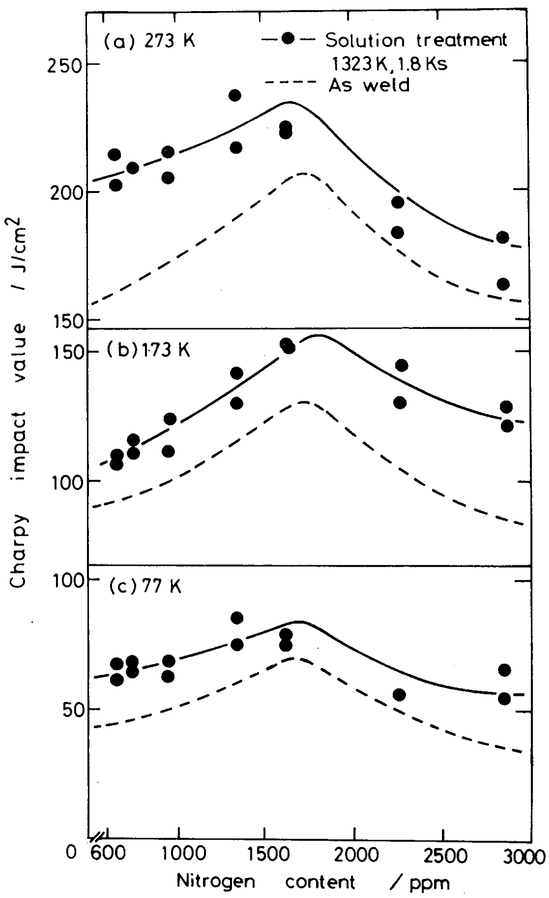

Fig. 12 Effect of nitrogen content on the charpy impact value of the weld metals (as welded and solution treated) at the various test temperatures. (a) 273K, (b) 173K, (c) 77K.

(b) 173K and (c) 77K are shown in **Figure** 12. Dotted lines in the figure indicate the results on as welded specimens. The charpy impact values increase with increasing of $\underline{N}$ content of weld metals. And charpy impact value shows a maximum value at $\underline{N}$ content 1700 ~ 1800 PPM approximately.

This treands are similar to those of as welded specimens.

From these results, it may be thought that charpy impact values are not influenced by δ-ferrite content of weld metals in this experiment.

It is estimated that excellent impact properties are caused by nitrogen content mainly. Discussion will be carried out on that cause at the later.

The nitrogen dissolved into γ phase in weld metals without evolution or making a blow hole because of the rapid cooling on the welding thermal cycle. But, in this study, nitrogen apparent of nitride must be considered in nitrogen content upper than 1800 PPM.

To clarify the state of nitrogen, the lattice parameter of γ phase are measured. Relation between lattice parameter and nitrogen content is shown in **Figure** 13. The lattice parameters are enlarged by nitrogen containing up to approximately 1600 ~ 1700 PPM.

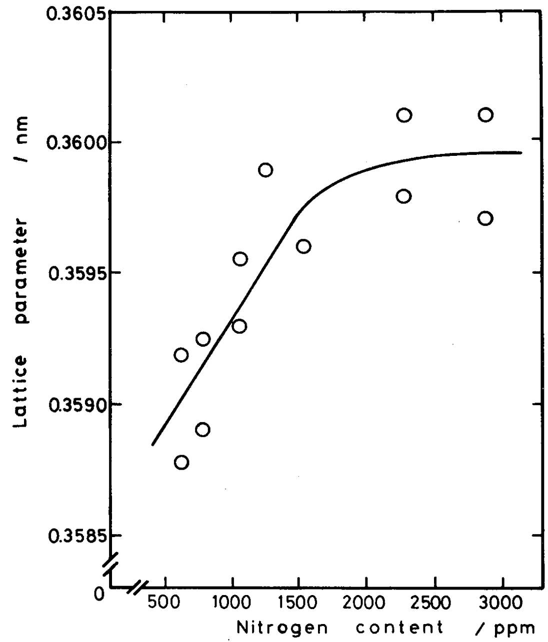

Fig. 13 Change in the lattice parameter of the austenitic matrix of weld metal with nitrogen content.

It is estimated that nitrogen dissolved into γ phase up to 1600 ~ 1700 PPM, but increasing with nitrogen content further, precipitations of nitrides (clasters) may be formed.

Consequently, the changing of hardness in the Fig. 3 is due to solution hardening of nitrogen.

The effect of solution hardening of weld metal on the plastic deformability is considered. It has been reported[9] that lateral expansion of impact tested specimen correspond approximately to impact values at cryogenic temperature of the stainless steel weld metals.

The large value of lateral expansion means a good plastic deformability.

Measurements of lateral expansion are carried out on the ruptured specimens. The lateral expansion increases slightly increasing with nitrogen content. This result means that the solution hardening of weld metals has a good effect on the weld metal toughness.

On the bad effect of nitrogen on impact properties is studied. The weld metals whose impact value decreased with increasing of nitrogen content had several characteristic properties such as (1) microstructure is single γ phase. (2) fracture morphology shows intergranular fracture with brittle failure. (3) lattice parameter becomes to approximately constant.

It is said that fully austenite stainless steel weld metal is susceptible to hot cracking (microfissuring) during solidification.

Microfissuring bend test has been carried out on the weld metals by refering to Lundin's paper[10]. The fissure bend test employs a multirun, double-layer, weld pad to evalution of fissuring. The weld pad is deposited on the base plate (12 mm thick, 50 × 200 mm).

After grinding on the weld pad surface to plane, bend test was performed on the weld pad to the included angle of 120 degree in a fixture. Fluorescent penetrant testing was performed to detect the microfissuring on the bended surface. Microfissures were detected from the specimens containing nitrogen approximately 2300 PPM and 2800 PPM. (Number of fissure $10 \sim 30$, total cracking length approximately 8 mm vs measured area 50 × 60 mm).

It is estimated that the impact value of weld metal decreased with increasing of these microfissures.

On the other hand, it is considered that the nitrogen in the weld metal makes precipitation of nitride.

Transmission microscope observation was performed on high nitrogen content weld metals.

In case of the present study, nitride were not detected by TEM. And then the inclusions of the weld metals are examined closely.

Intermetallic inclusions are extracted from weld metals by using speed method[11].

The extracted residues are analyzed by fluorescence X-ray analyzer, and relation between Cr content in the extracted residues and nitrogen content of weld metal are studied.

The integrated intensity of $Cr_{K\alpha}$ was increased with increasing of nitrogen content. The Cr-nitride may be exist in the extracted residues by considering of these results.

In brief, it is estimated that the nitride tends to precipitate intergranularly along grain boundaries and causes the intergranular brittle fracture.

The similar results are reported by T. Ogawa et al.[12] on the high nitrogen weld metal made by GMAW or GTAW process.

4. Conclusions

The 7 kinds of the stainless steel SMA electrodes (lime-titania type) contained varying amounts of Mn-nitride or Cr-nitride in the covering were provided. The weld metals are made by SMAW process using these covered electrodes. Relation between microstructure, low temperature impact properties of weld metal and nitrogen content of weld metals are investigated.

The main results are summarized as follows.

1) Nitrogen has the most significant effect on the δ-ferrite content of weld metal.
2) Impact value of weld metals increases with increasing of the nitrogen content of weld metals up to approximately $1700 \sim 1800$ PPM after then the impact value falls as the nitrogen further increased.
3) δ-ferrite and strain-induced martensitic structure of weld metals have not hardly influenced to impact value of weld metal in this study.
4) The strengthening mechanism of weld metals due to addition of nitrogen is estimated that the effect of austenitic structure stabilized and interstitial solution hardening. The precipitation of nitride in the excese nitrogen containing weld metals decreases the impact value of weld metals. And, also increasing of the microfissure decrease to impact value of weld metals.
5) Nitrogen content up to approximately $1700 \sim 1800$ PPM of weld metal which is introduced by SMAW process gives a good influence on the impact properties at low test temperature under condition of this study.

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