Effect of Nitorogen Content on the Low Temperature Mechanical Properties of Type 304 Austenitic Staninless Steel Weld Metals†

Toshio ENJO* Yasushi KIKUCHI** and Hiroshi NAGATA***

Abstract

High-nitrogen austenitic stainless steel weld metals are obtained by using type 304 electrode wire (1.6mmø) and N_2-Ar mixture shielding gas.

Low temperature tensile and impact tests on deposited metals are carried out at test temperature range from 0°C to −196°C.

The main experimental results are summarized as fellow:

Nitrogen content of weld metals increase considerably with increasing of N_2 volume percent in shielding gas, then at 100% N_2 shielding, nitrogen contents show the about 0.2wt%.

A cast structure contained δ-ferrite is obserbed in the weld metal as weld condition but content of δ-ferrite decrease with inceasing nitrogen content of weld metals. There is no δ-ferrite in the weld metals which contained about 0.18wt% nitrogen. 0.2% proof stress increase with incresing of nitrogen content of weld metals. This tendency is obserbed clearly as the test temperature depression, and this behavior is discussed by bearing on the strain-induced martensitic transformation in the weld metal at low test temperature.

The tensile strength of weld matals increase as the test temperature depression but is not changed by nitrogen content of specimens.

At impact test, the absorbed energy of weld metals slightly increase with increasing of nitrogen content of weld metals.

The effect of nitrogen on the absorbed energy of high-nitrogen weld metal is changed by welding method and source of nitrogen to weld metals.

It is know that high-nitrogen type 304 austenitic stainless steel weld metals hold a high proof stress without decreasing of the toughness at low test temperature.

KEY WORDS: (Nitrogen) (stainless steel) (MIG Process) (Mechanical Properties) (Low Temperature)

1. Introduction

A study of alloying nitrogen with the iron base alloys has been examined by many investigaters, and then nitrogen has been made a practical application of improvement in some of heat resisting alloys.

For example, alloying nitrogen with some austenitic stainless steel as type of 304 and 316 appears to be one means of improving on elevated temperature strength. Recently, 304 or 316 type austenitic stainless steel with about 0.1~0.3wt% N can be used and are normalized by JIS.[1)]

Thus, commercial applications have been made on alloying element for some stainless steel plates but the effects of nitrogen on the welds or welding process do not make cleair yet.

Nitrogen dissolves interstitially in austenite and it is the strong austenite stabilizer while it easily conbines with the element (such as Cr, Ti, Zr, Nb, Si and so on) in the steels to form a nitride.

So, in the welds which are heated by weld thermal cycle, the effects of nitrogen on the various properties of steels must be considered in separated into two type of nitrogen as the soluble nitrogen or nitrogen in nitride.

SUS304 or316 type austenitic stainless steels show the good mechanical properties at low temperature and extensive use of low temperature survice in industry such as for LNG storage tanks etc, those austenitic stainress steel for structural materials have played a prominent role. But it is known that, at tensile test, 0.2% proof stress is low level.

This study has been made to determite the effect of nitrogen on the MIG welding process of high-nitrogen austenitic stainless steel plate,: the high-nitrogen 304 austenitic stainless steel weld metals are made by MIG welding process and specimen from weld metal are tested by tensile or impact test machine at low temperature. On the foundation of these results, the effect of nitrogen cotents of weld metals on the 0.2%

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proof stress, U.T.S., absorbed energy, microstructures and strengthening mechanism due to nitrogen are investigated.

2. Experimental Methods

2.1 Materials used

Type 304 austenitic stainless steel base metal ($12^t \times 70 \times 150^{mm}$) and electrode wire (1.6mmø) are used in this investigation. The chemical composition of these materials are shown in **Table 1.**

Table 1. Chemical compositions of base plate and electrode wire.

	Chemical composition (wt%)							
	C	Si	Mn	P	S	Ni	Cr	N
Base plate	0.06	0.62	0.99	0.029	0.005	8.46	18.23	0.048
Electrode wire	0.02	0.47	2.07	0.026	0.005	9.90	20.10	0.023

2.2 Composition of shielding gas

The welding was parformed under N_2-Ar mixture gas shielding. High-nitrogen austenitic stainless steel weld metals are obtained by reaction between shielding gas and molten weld metals under the arc welding process. Nitrogen cotents of sound weld metals were cotrolled by changing of nitrogen volumetric percent in shielding gas.[2-3]

2.3 Welding procedure

SIGMA type welding apparutus have been assembled by using carbon-dioxide semi-automatic welding machine. After setting the base metal and the electrode wire which were surface ground and cleaned, 60° Vee butt welds were made by multipass welding automatically in flat position using a constant potential rectifier as the welding source with an electrode positive polarity.

Welding variables used are: arc voltage 27V, welding current 300A, and welding speed 20cm/min. All deposited metal tensile test specimens (6mmø, with screw), charpy impact test specimen (JIS. No.4 type) and samples for chemical analysis were taken from 12mm thick 60° Vee butt welds as shown in **Fig. 1.**

The chemical analysis of nitrogen in the weld metals were made by Kjeldahl distillation method. Microscopical observation and delta ferrite cotent measurements were made on weld metals. The mechanical tests have been carried out mainly at the teperature range from 0°C to −196°C (Liquefied nitrogen).

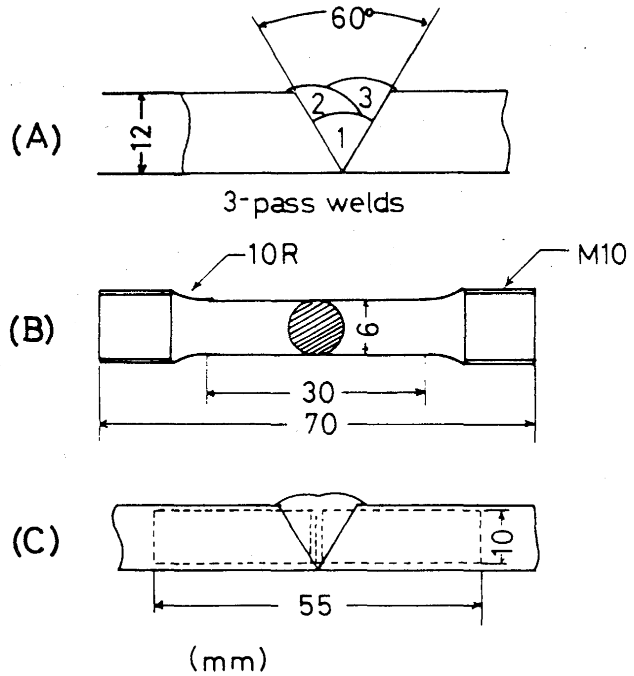


Fig. 1 Location of test specimen, (A) Groove angle and profile of cross section, (B) Tensile test specimen, (C) Impact test specimen.

3. Experimental Results

3.1 Nitrogen cotent (N) of weld metals

Austenitic stainless steel weld metals which nitrogen content (N) are controlled were obtained by changing of nitrogen volmetric percent (vol.%) in N_2-Ar mixture shielding gas. **Figure 2** shows the relation between nitrogen content of weld metals (N) and nitrogen vol.% in shielding gas. The welding variables are indicated in the same figure.

In order to check the segregation of nitrogen in weld metals, samples from the various parts of multi pass weld metals were analyzed, but the segregation of nitrogen was not observed. The analitical values obtained in the present study are from the final pass of the welds. Nitrogen content of weld metals increase considerably with increasing of N_2 Vol.% in shielding gas, then at pure N_2 shielding (100% N_2), nitrogen

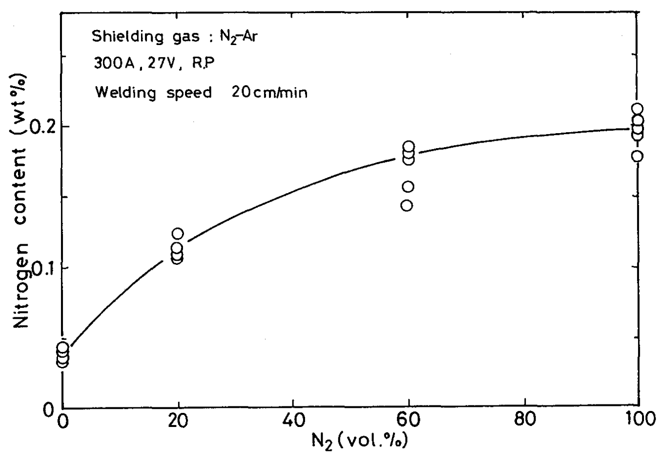


Fig. 2 Relation between nitrogen content of weld metal and N_2 volumetric percent in shielding gas.

contents show the about 0.2wt%. This result is similar tendency to previous papers.[5)]

The weld defects such as porosity, inclusions etc, are examined by optical microscope.

Even if the ratio of N_2 and Ar in the shielding gas was changed, the content of alloying elements in the weld metals such as Ni, Cr, Mn, Si etc were not changed.

3.2 Structures of weld metals

Microstructure of weld metals were affected largely by compositions of shielding gas.

The weld metals ($\underline{N} \fallingdotseq 0.038$wt%) made in 100% Ar shielding gas showed the structure of two phase (δ-ferrite + austenite). The δ-ferrite existed as network situation in the austenite and it was suddenly decreased with increasing of N_2 vol.% in shielding gas.

The δ-ferrite content was determined by point count method. Relation between δ-ferrite content and $\underline{N}$ content is shown in **Fig. 3**.

Using pure Ar for shilding gas, weld metals had about 13~14% δ-ferrite but it was known that the weld metals became δ-ferrite free structure in case of $\underline{N}$ content is more than about 0.18wt%. This δ-ferrite gives an effect to weld metals on the mechanical property.

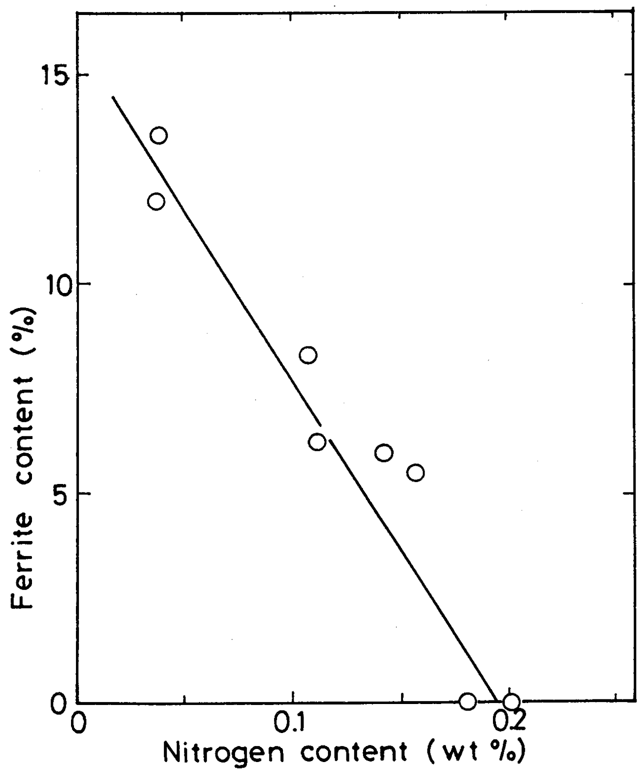


Fig. 3 Relation between nitrogen content of weld metal and δ-Ferrite content in weld metal (as weld condition).

3.3 Mechanical properties of weld metals

3.3.1 *Results of tensile test*

Instron type universal testing machine with low temperature chambar was used for low temperature tensile test. The specimen was cooled to various test temperature in the chamber using various coolants, and then it was tested by cross head speed 1mm/min, after holding for 20min at test temperature.

The test temperature was cotrolled a range at ± 2°C. The effects of nitrogen content ($\underline{N}$) in weld metals on tensile stregth (U.T.S) and 0.2% proof stress at room temperature are shown in **Fig. 4.** It seems that 0.2% proof stress and U.T.S of weld metals are not hardly influenced by nitrogen cotent ($\underline{N}$) (up to 0.2wt%), and the weld metals have 0.2% P.S. of 38~40kg/mm^2, U.T.S. of 66~68kg/mm^2 respectively.

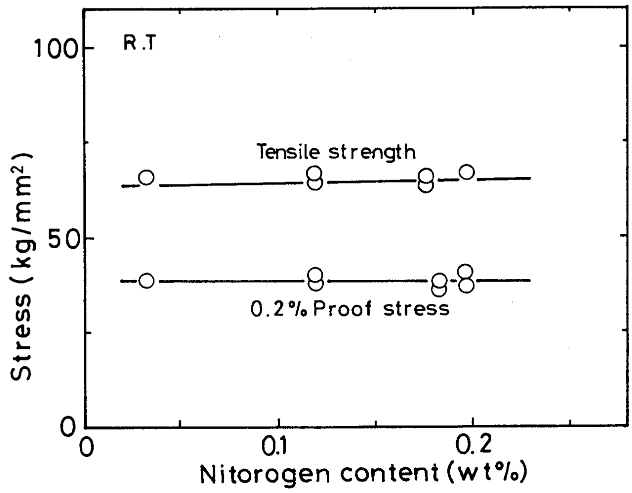


Fig. 4 Effect of nitrogen content on the tensile stregth and 0.2% proof stress of weld metal.

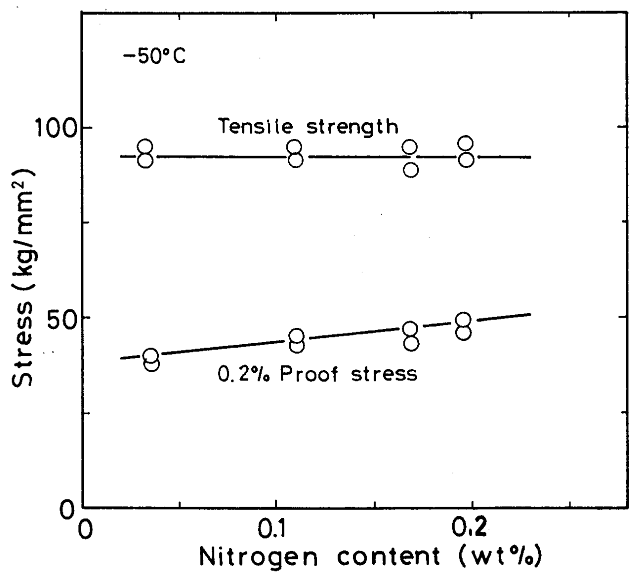


Fig. 5 Effect of nitrogen content on the tensile stregth and 0.2% proof stress of weld metal.

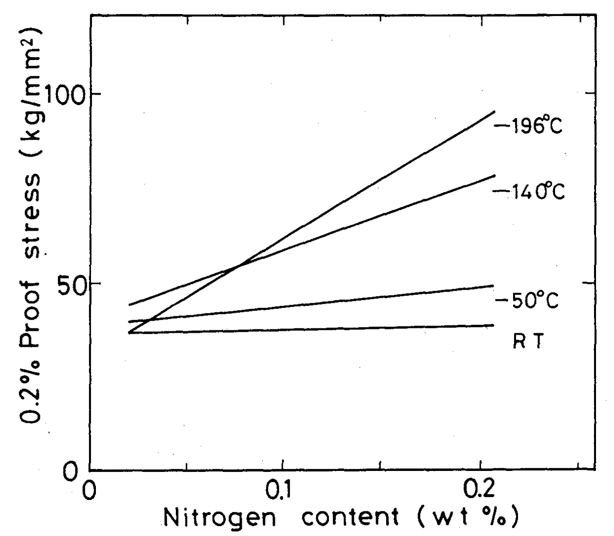


Fig. 6 Effect of nitrogen content on the 0.2% proof stress of weld metal at various test temperature.

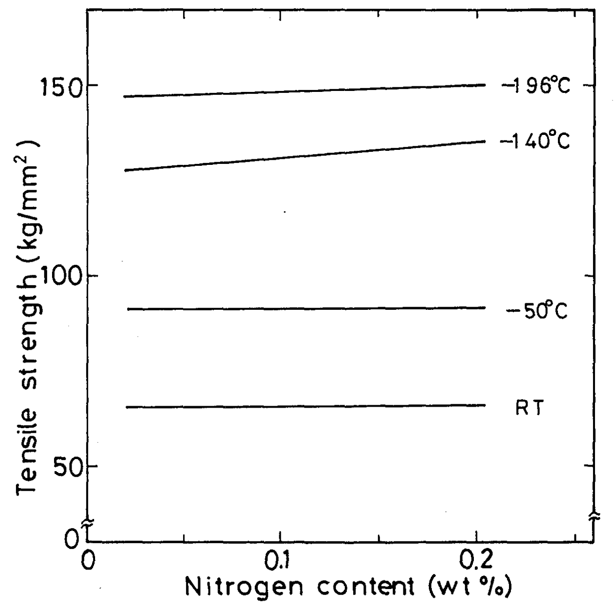


Fig. 7 Effect of nitrogen content on the tensile stregth of weld metal at various test temperature.

The test results at $-50^{\circ}C$ are shown in **Fig. 5.** 0.2%P.S. increases with increasing of N cotent in weld metal, i.e. it increases to about 51kg/mm^2 at 0.2wt% N.

U.T.S. value are the larger (about 92kg/mm^2) than that (68kg/mm^2) of obtained at room temperature and they are not so changed by nitrogen content.

Summary on 0.2% P.S. on weld metals tested in various test temperatures are shown in **Fig. 6.** The 0.2% P.S. of specimens contained high nitrogen increased with decreasing of temperature. An addition of nitrogen to weld metals have a remarkable effects on P.S. of weld metals at low temperature. This effects are reported on the wrought austenitic steel by Ōnishi[6] and Mukai[7]. Summary on tensile test results of weld metals specimens are shown in **Fig. 7.** It is

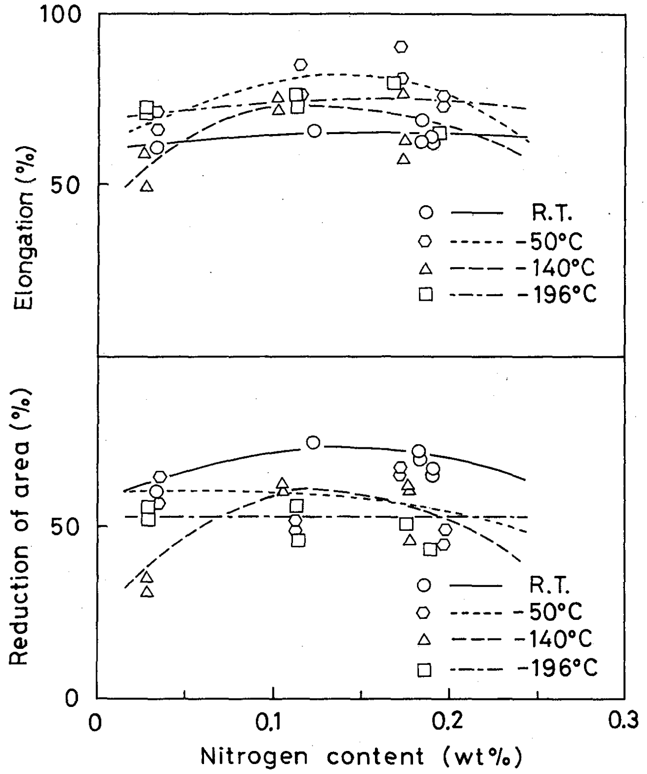


Fig. 8 Effect of nitrogen content of weld metal on the elongation and reduction of area of weld metal at various test temperature.

known that tensile strength increase with decreasing of test temperature. It increase to about 153kg/mm^2 at $-196^{\circ}C$. It is became evident that the tensile strength are not hardly influenced by nitrogen content in the limit of this experiment. Elongations and reduction of areas on the specimens are summarized in **Fig. 8.** Elongation are 55~60% at room temperature and increase slightly with decreasing of test temperrature. Reduction of areas are 60% at room temperature, and also decrease with decreasing of test temperature.

The stress-strain curves on low nitrogen content specimens obtained at the low test temperature are serrated with small.

It is considered that during the deformation process of specimen some transformations occur. Microscopical ovservation of the ruptureal specimens have currid out and martensitic structures are found.

3.3.2 Results of charpy impact test

Impact test have been carried out at temperature range from $-196^{\circ}C$ (liquefied nitrogen) to $600^{\circ}C$. As shown in Fig. 1, Vee notch was machined at the center of weld metals so as to the fracture surface and longitudinal direction of bead become paralel to each other.

When such low test temperature as $-50^{\circ}C$~ $-196^{\circ}C$ are required, liquefied nitrogen, dryice and other coolant are used. The specimens were cooled in the cooling chamber to the test temperatures. High temperature impact test specimens are heated by electric furnace.

After holding for 20min at the test temperature, the specimen was setted to the tester and it was ruptured within three seconds. The test results at 400°C and −50°C are shwn in **Fig. 9**. At both test temperature, the absorbed energy values of weld metals increases with increasing of N content in the weld metals.

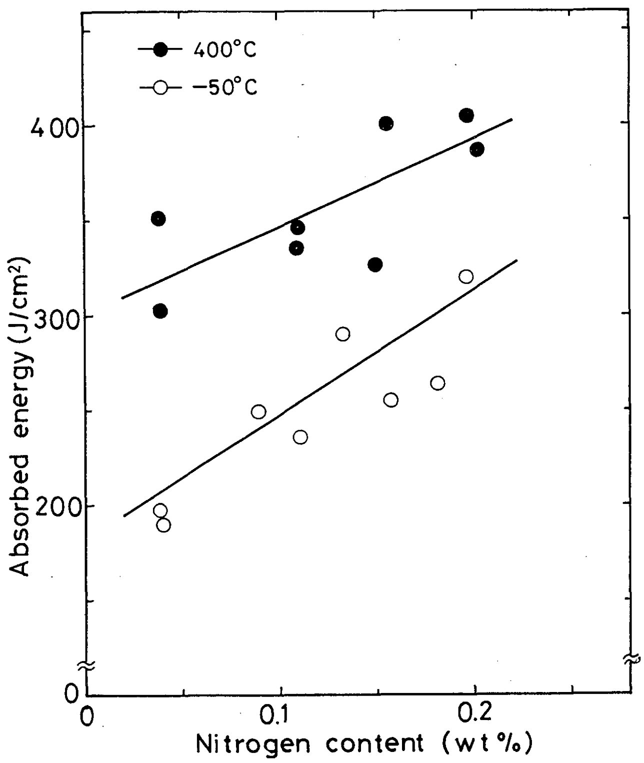


Fig. 9 Effect of nitrogen content on the absorbed energy of weld metal.

The test results at 400°C, weld metals have the absorbed energy value of about 320J/cm^2 at 0.03wt% N content and about 410J/cm^2 at 0.2wt%N content respectively.

Absorbed energy value tested at −50°C are the smaller than that of obtained at 400°C and it was changed by N content and about 410J/cm^2 at 0.2wt% N from about 200J/cm^2 (N ≒ 0.03wt%) to about 320J/cm^2 (N ≒0.2wt%).

Summary on absorbed energy values of weld metals tested in various test temperatures are shown in **Fig. 10**. In all testing temperature range, the high nitrogen weld metal specimens have a large absorbed energy value. The effect of nitrogen on the absorbed energy value of weld metal which are determained by impact test is recognized clearly at low test temperature.

As weld condition, the weld metals have the cast structures but its toughness is approached to the absorbed energy values of base metal with increasing of N content in weld metals. Test temperature above 300°C, the weld metals have the larger absorbed energy than that of base metal and an effect of nitrogen content on the high temperature strength is showed remarkably.

The relation between and δ −ferrite content in weld metals is studid, and it is known that absorbed energy value of weld metals decrease with increasing of δ −ferrite content.

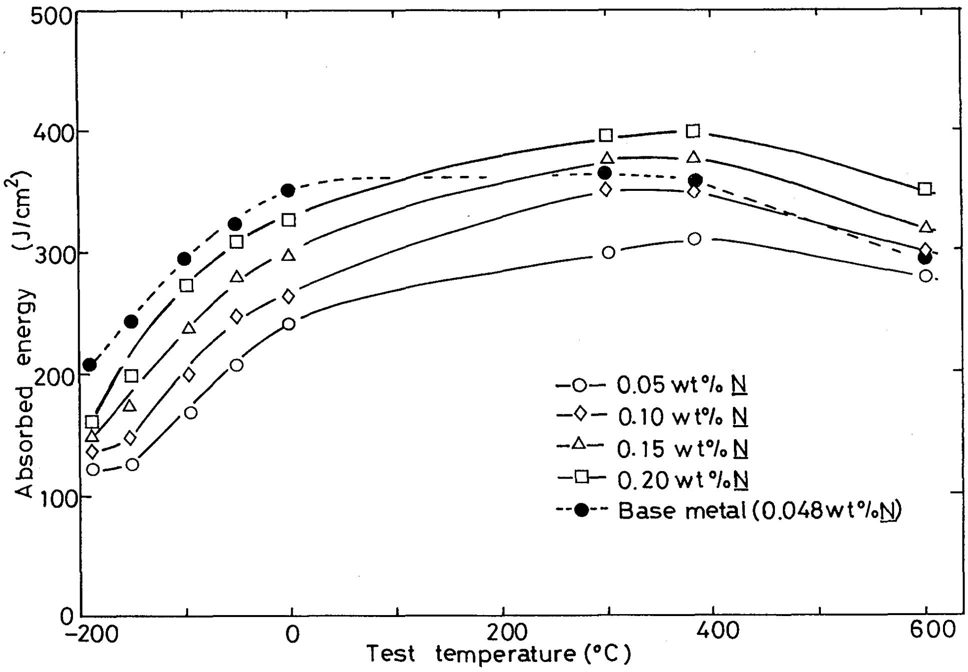


Fig. 10 Effect of nitrogen content on the absorbed energy of weld metal at various temperature.

4. Discussions

4.1 The influence of nitrogen on the proof stress and absorbed energy value of weld metals

As show in the test results, it is known that addition of nitrogen to the weld metals is efficiency to 0.2% proof stress and this increasing of strength occures without decreasing of the toughness.

It is well known that strain-induced martensitic structure is formed when austenitic steel is deformed at low temperature. During deformation process, stress concentrations in the specimen are occurred, but these stress concentrations by the deformation may be relieved by strain induced martensite transformation. It means that they are deformed with great facility[8–9].

In this study, it is cleared that the weld metals are strongly stabilized by dissolved nitrogen.

Consequently, high-nitrogen contained austenitic stainless steel weld metals are not subject to transforming from austenite to martensite structure than that of low-nitrogen contained weld metals.

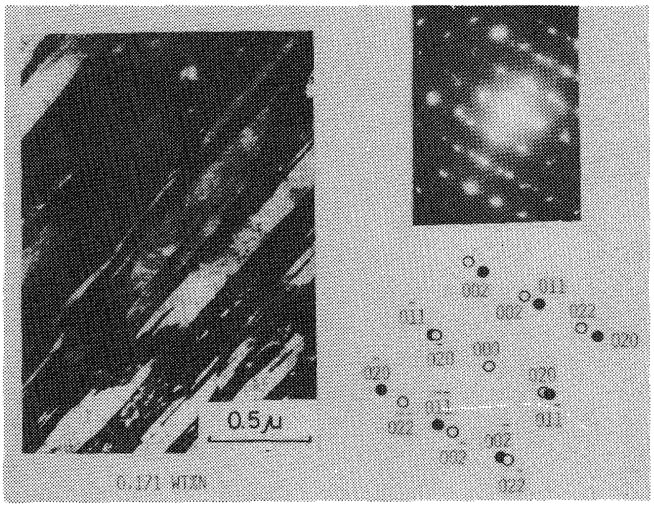
Increasing on 0.2% proof stress of tensile test in the high-nitrogen weld metals was discussed from the stand point of martensite transformation of austenite which is produced by low temperature tensile test.

As an example, the strain induced martensite strucuture of the specimen with 0.17wt% nitrogen is shown in Photo.1 and this metallographic obsevation was carred out by electron microscope on the specimen ruptured by tensile test at −196°C.

X-ray diffraction analysis was used for quantitative determination of martensitic structure in the specimeans ruptured by tensile test at various test temperature, but the quantity of martensitic structure could not determined exactly.

Thus, apparent degree of martenstitic transformation (M/Mmax) of ruptured specimens was determined.

Here, M: intergrated intensity of (200) α' diffraction pattern on the specimens ruptured at various test temperatures. Mmax: integrated intensity of (200) α' diffraction pattern of the lowest nitrogen content specimen ($\underline{N} \fallingdotseq 0.037$wt%) in this study ruptured at −



Test Temp. -196°C (100)

Photo 1. Transmision electron micrographs of specimen ruptured at −196°C by tensile test.

Table 2. Effect of welding method and source of nitrogen to weld metal on the absorbed energy of weld metal.

type	ferrite number FN	nitrogen content N wt%	absorbed energy Kg-m	welding process	source of nitrogen	reference
316L	-1	0.033	5.2	SMA	nitrogen enriched metal powders	E.R.szumacowski et al W.J.,58 (1979), No. 2
		0.055	4.1			
308L	-1	0.04~0.05	5.7	SMA	nitrogen compounds	N. ikeda, S.shin et al preprints. N.M.of J.W.S. No.25 (1979)
		0.07~0.10	4.6			
		0.11~0.13	4.1			
316	-5	0.24	7.1	MIG	gaseous nitrogen	T.kobayashi, T.enjo et al J.H.T.S., vol.7 (1981) No. 2
304L	8	0.05	9.5	MIG	gaseous nitrogen	this study
	6	0.10	10.8			
	-1	0.19	12.8			

Test Temp. -196°C

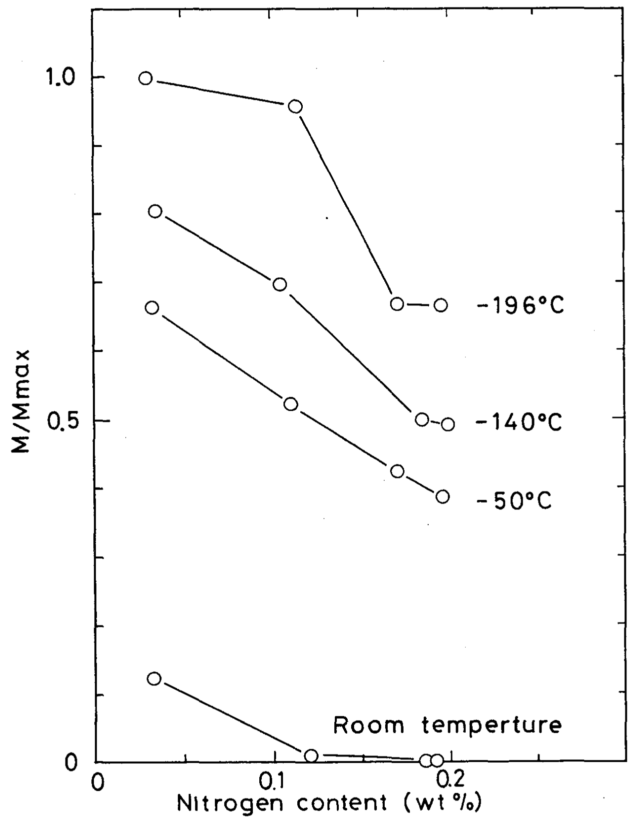


Fig. 11 Relation between nitrogen content of weld metal and apparent degree of martensitic transforation (M/Mmax).

196°C. This specimen showed the largest integrdted intencity.

An interaction of test temperature and nitrogen content on M/Mmax value are summerized in **Fig. 11.**

It is known that values of M/Mmax are increased with decreasing of the test temperature and decreasing of nitrogen content. It can be speculated that dissolved nitrogen stabilizes the austenite strongly and hinders the transformation of austenite to martensite during the deformation process.

This fact is related to prevent the relaxation of stress concentration depending on martensite transformation of austenite, and so this fact is effective to increasing of 0.2% proof stress.

Relation between 0.2% proof stress and M/Mmax is shown in **Fig. 12.** These results show the linear relationship. The 0.2% P.S. increased with decreasing of M/Mmax value. It has been estimeted that the quantity of martenstite transformation by deformation decreased with increasing of nitrogen concentration in austenite and 0.2% P.S. increased by dissolved nitrogen in austenite. Changing of proof stress is discussed from the standpoint of strain induced martensitic transformation in austenite. It attracts attention that in the study the martensitic structures are observed on ruptured specimens but changing of proof stress of specimen is occured during elastic deformation process.

The authors have been thought that the relation between martensitic transformation and behavior of proof stress has to be studied moreover and to be discussed exactly.

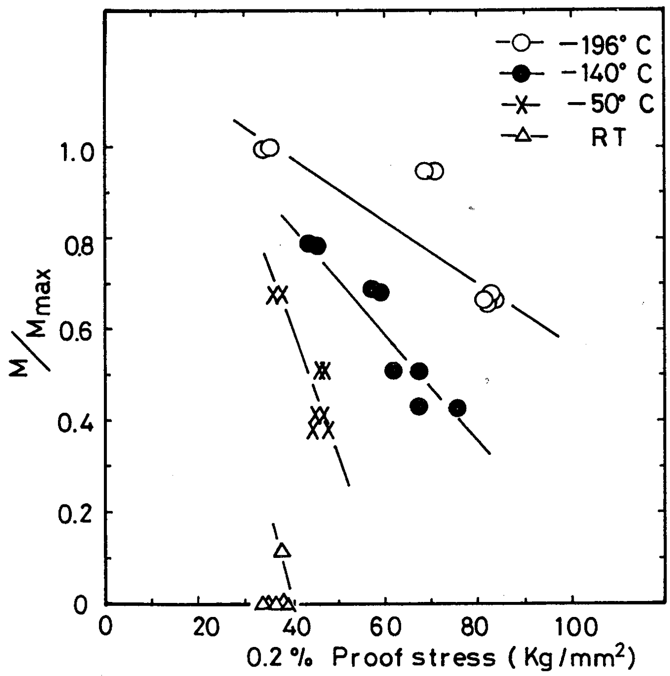


Fig. 12 Relation between 0.2% proof stress and M/Mmax.

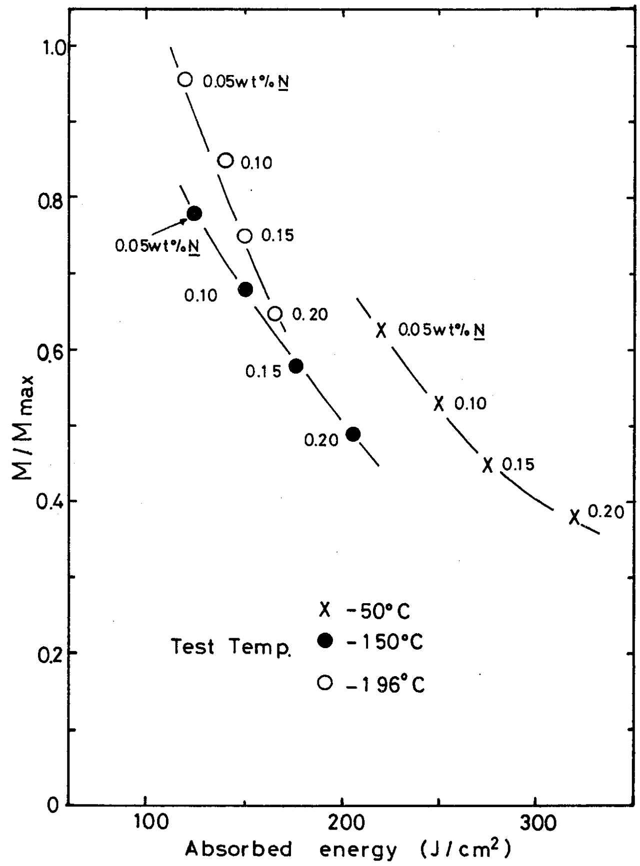


Fig. 13 Relation between absorbed energy and M/Mmax.

As previously described, ultimate tensile strength of weld metals were not changed by N content in weld metals. On the low nitrogen weld metals, it is seemed that the effect of δ -ferrite on the strengthing of weld metals is considered and consequently U.T.S. have a constant values in this study.

Relation between impact test results and apparent degree of martensitic transformation (M/Mmax) is shown in **Fig. 13.** Results obtained at −150°C and −196°C are not shown in sensible order of test temperature, but the same lirear relationship is observed. Absorbed energy of specimen increased and M/Mmax decreased with increasing of N content of weld metals respectively. It was known that the austenitic structure stabilized by nitrogen have a good toughness.

4.2 Influence of welding method and source of nitrogen to weld metals on the toughness of weld metals

Some investigaters have their own opinion for the effect of nitrogen content various type of austenitic stainless steel weld metals on the toughness at low temperature (−196°C) and their results[10-11] are summarized in Table 2. E. R. Szumachowski etal[10] and Ikeda and Shin[11] reported their experimental results on the type 316 or 308 weld metals but the chemical compositions of weld metals used in their study is not same that of the present study. The Ferrite number (F.N) is calcurated according to equation reporteal by E.R.Szumachowski[10].

This results show cleary that, the toughness of weld metals decrease with increasing of N content of weld metals, and this tendency between toughness and N content is not same as that of the present study. The different experimental procedures from this study have been used such as, shielded metal arc welding prcess was used. And so nitrogen content of weld metals was adjusted by additions of nitrogen-enriched metal powders or nitrogen compounds used to the electrode covering. It is estimate that the state of nitrogen in the deposited metal by S.M.A differ from that of the MIG process such as using N_2-Ar mixture shielding gas.

Whether it is true or not this fact is very interesting, and then the discussion on these problems have to carry out in future.

5. Conclusion

High-nitrogen austenitic stainless steel weld metals are obtained by using type 304 electrode wire base metal and N_2-Ar mixture shielding gas. Effect of nitrogen content on the low temperature mechanical properties of weld metals is examined by tensile and impact test.

Main results obtained as fellows.

1) nitrogen content of weld metals can be controlled within the limits of 0.2wt% by changing of nitrogen volumetric percent in shielding gas. There is no δ -ferrite in the weld metals which contained about 0.18wt% nitrogen.
2) The tensile strength of weld metals increase with decreasing of test temperature, but is not changed by nitrogen content within the limit of this experimental conditions.
3) 0.2% proof stress of weld metals increase with increasing of nitrogen content. This tendency is obserbed clearly at the low test temperature, and this behaviour is discussed by the standpoint according to hindering effect of the strain-induced martensitic transformation in the austenitic structure stabilized by nitrogen.
4) In the impact test, the absorbed energy of weld metals slightly increase with inncreasing of N content.
5) The effect of nitrogen on the toughness of weld metals is changed by welding method and source of nitrogen to weld metals.
6) Dissolved nitrogen in type 304 austenitic stainless steel weld metals which is introduced by MIG process gives a good effects on the mechanical properties such as high-proof stress and good toughness at low temperature.

Aknowledgments

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