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Weldability of High Nitrogen Stainless Steel†

WOO Insu* and KIKUCHI Yasushi**

Synopsis

The purpose of this paper is to give a short survey of the influence of nitrogen in stainless steel welds. The review covers: the levels of nitrogen in weld metal, the influence of nitrogen on stainless steel weld metal characteristics such as weld defects, corrosion resistance and mechanical properties. High nitrogen steel welding must consider the risk of nitrogen escape from the weld pool. Avoiding nitrogen losses may be accomplished by controlling the shielding gas, welding parameters and the compositions of filler metal. An increase of nitrogen in the weld metal decreases the δ-ferrite content. The reduction of δ-ferrite in austenitic weld metals will result in an increase in the solidification cracking susceptibility. However, the role of nitrogen in affecting the solidification cracking susceptibility of fully austenitic weld metals is unclear. Nitrogen additions increase the pitting corrosion resistance in weld metals whereas they decrease resistance to stress corrosion cracking because of δ-ferrite reduction. Nitrogen also improves mechanical properties in weld metals. However, the presence of nitrides may be detrimental to the mechanical properties of stainless steel welds.

KEY WORDS: (high nitrogen stainless steel) (weld defects) (corrosion resistance) (mechanical properties) (nitride)

1. Introduction

High nitrogen stainless steels (HNS) have been used in the electronics, the precision and the cryogenic industries etc because they are considered to be high strength, high ductility and toughness materials[1-5]. For example, a new material of cold-rolled austenitic stainless steel containing over 1wt% of nitrogen is a candidate.

A wider use of HNS is, apart from other features, dependent on their joining characteristics, i.e., mechanical properties, and corrosion resistance. In welding of HNS it is, for all of the reasons given above, essential to avoid nitrogen losses, weld defects and nitride precipitation etc which could result in loss of corrosion resistance as well as mechanical properties (see **Fig.1**). Clearly, the influence of nitrogen in stainless steel welds is a complex and less studied phenomenon than it is in base metal.

This paper attempts to put the available information on the influence of nitrogen in stainless steel welds in perspective. The review initially deals with the levels of nitrogen that are normally encountered in iron and stainless steel welding and then discusses the influence of these levels on important stainless steel weld metal characteristics such as weld defects, corrosion resistance and mechanical properties.

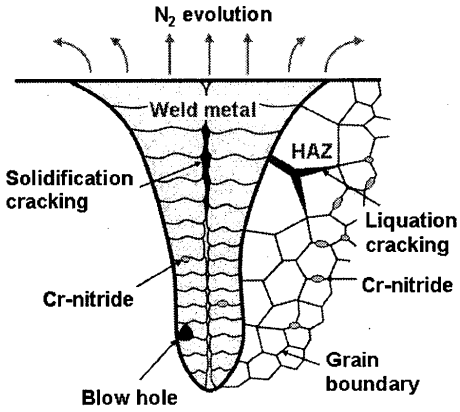

Fig.1 Schematic illustration of a high nitrogen steel weld

2. Nitrogen absorption in weld metal

A schematic representation of the nitrogen absorption via atomic nitrogen from a moving weld pool is shown in **Fig.2**[6]. There are four ways in which nitrogen can dissolve in liquid iron: molecular, atomic, ionic and as NO gas. The nitrogen concentration remaining in the solidified weld metal represents a balance between nitrogen absorption, which is dominated by one of the faster processes-atomic ionic or NO gas and the evolution of nitrogen by bubble formation.

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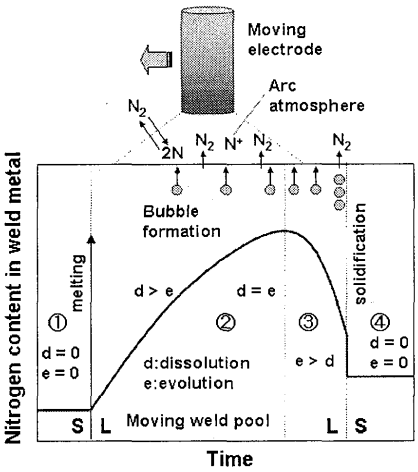

Fig.2 Schematic illustration of the weld metal nitrogen content under a moving welding arc in an atmosphere containing nitrogen gas (N2) : Stage 1: premelting stage, Stage 2: arc melting with dissolution dominating. Saturation (i.e., d=e)may or may not be reached. Note that d=e is a time independent condition and not necessarily a thermodynamic equilibrium condition, Stage 3: Weld metal cooling (still liquid) with decreasing saturation solubility and evolution dominating (bubble evolution may prevail), Stage 4: Solidification with step change in solubility and consequent rejection of nitrogen with excess causing porosity, accompanying nitrogen in solid solution.

According to Pehlke and Elliott[7], among others, the equilibrium solubility of N_2 in liquid iron is dependent on the reaction:

$$\frac{1}{2}N_2\ (\text{gas}) \rightarrow \underline{N}\ (\text{dissolved in liquid iron})$$

The reaction constant is given by

$$K = a_N / \sqrt{ppN_2} = f_N[\underline{N}]/\sqrt{ppN_2}$$

, where a_N is the nitrogen activity, ppN_2 is the partial pressure of nitrogen and f_N is the activity coefficient. At small nitrogen concentrations f_N=1, where [N] is the nitrogen concentration in liquid iron; then

$$[\underline{N}] = K(ppN_2)^{1/2}$$

The equilibrium solubility of nitrogen in iron for non-arc melts at one atmosphere is given by:

$$[\underline{N}] = 0.0565\exp(-860/RT)wt\%$$

Assuming that the temperature of the welding pool is 1873K, the theoretical equilibrium nitrogen content is around 0.045wt%. General rules of absorption behavior established with iron can then be extended to those for stainless steel weld metal, by taking into account the influence of alloying elements as well as the non-equilibrium conditions that prevail during welding. For stationary GTA (gas tungsten arc) welding above iron small piece, nitrogen levels in the weld metal obey Sievert's law up to pressures of 3-4$\times 10^{-3}$ atmosphere (0.5-0.6 $atm^{1/2}$) of nitrogen (see **Fig.3**[8]). At these pressures the nitrogen content is around 0.06wt%, i.e., the solubility is about 20 times that predicted by results obtained from non-arc melts. In addition, it is interesting that experiments with moving work pieces for both the

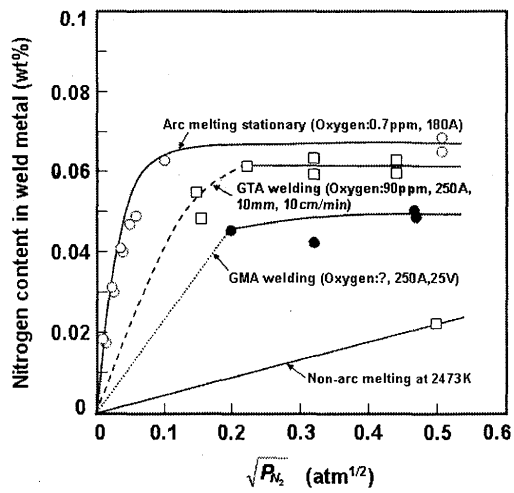

Fig.3 Nitrogen absorption by iron under various melting conditions for nitrogen additions to a one atmosphere argon shield.

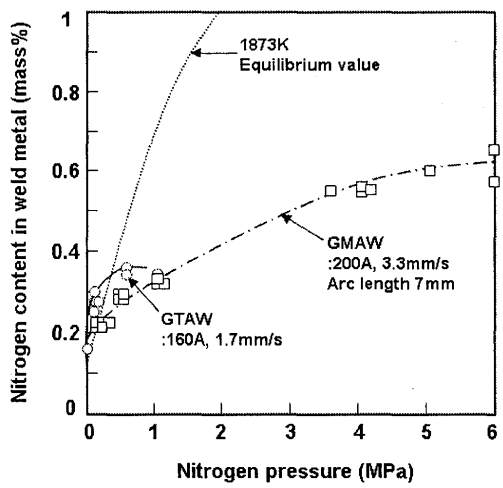

Fig.4 Nitrogen absorption by SUS316 weld metal under GTA and GMA welding processes.

GTA and GMA (gas metal arc) welding processes, produce similar trends as observed for stationary arc melts. At low pressures these again produce weld metal nitrogen levels many times higher than those of non-arc melts. Differences between the arc and the non-arc results (reaction constant and saturation level) may well be associated with variations in factors such as surface conditions, welding parameters, details of arc, etc.

On the other hand, investigations for pressures above one atmosphere are scarce. **Fig.4** indicates the nitrogen content in weld metal as a function of nitrogen pressure[9]. In the case of GTA welding, the value of the nitrogen content increases to 0.38wt% at 1.1MPa of nitrogen pressure. At a nitrogen pressure of over 1.1MPa, it is difficult to undertake GTA welding due to the consumption of the electrode, and the behavior of nitrogen absorption in weld metal can not be observed. However, GMA welding can absorb more high pressure

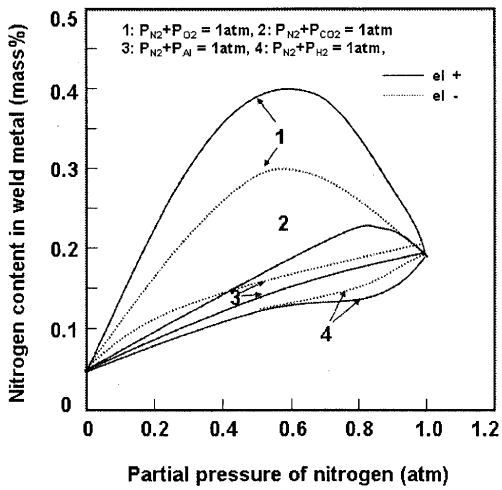

Fig.5 Effect of partial pressure of nitrogen in various carrier gases on the nitrogen absorption of stainless steel weld metal in MIG welding.

nitrogen than in the case of GTA welding. The nitrogen content increases with the pressure of 6.1MPa. As a result, it is clear that GMA welding presents more potential for nitrogen pickup than GTA welding.

2.1 Welding parameters affecting nitrogen absorption

Welding parameters, such as shielding gases, welding speed, arc current and arc voltage etc, are very important variables affecting nitrogen absorption in weld metal.

The nature of the gases in the welding atmosphere plays an essential role in nitrogen absorption. Oxidizing gases such as O_2 and CO_2 increase nitrogen absorption, whereas a reducing gas such as hydrogen decreases the amount of nitrogen absorbed into the pool. Nitrogen contents of up to 0.4wt% can be attained in the stainless steel weld metal depending on the nature of shielding gases and the partial pressures, as shown in **Fig.5** [10]. Kobayashi, et al.[10], reported that NO gas was generated in the arc, and detected NO gas in the arc atmosphere. Blake[11] and Den Ouden[12], also reported the generation of NO gas and then iron oxides formation [FeO] at the weld pool is given by:

$$2CO_2 + N_2 \rightarrow 2CO + 2O + 2N \rightarrow 2CO + 2NO$$
$$NO + [Fe] \rightarrow [FeO] + [\underline{N}]$$

This equation describes the possibilities of oxide layer formation, subsequent inhibition of nitrogen evolution, and enhanced nitrogen absorption.

An obvious increase of nitrogen concentration for MMA (manual metal arc) welding can be expected when the arc length increases, as shown in **Table 1**[13]. Schmidt, et al.[14], found an increase with R-type electrodes only, comparing medium and thick-coated rutile electrodes (R and RR symbolization). However, arc length has no significant effect on weld metal nitrogen levels for GTA welding on mild steel operating in pure nitrogen shielding gas, it is found that nitrogen contents remain unchanged as arc length is increased from 2 to 14mm[13]. Similar behavior applies to GMA welding over the voltage range 15V to 35V, also[15].

Table 1 Influence of arc length for R and RR type electrodes on the nitrogen content of weld metal.

Type	Visible Arc Length (mm)	%C	%Mn	%Si	%N
R	2	0.075	0.55	0.26	0.025
	4	0.069	0.48	0.23	0.041
	10	0.057	0.30	0.14	0.043
RR	2	0.075	0.55	0.42	0.035
	4	0.073	0.48	0.42	0.035
	10	0.072	0.38	0.20	0.036

The influence of welding speed on weld metal nitrogen contents has been systematically examined for GTA welding. According to Kuwana, et al.[16], for stainless steel, the nitrogen level almost doubles when speed is increased from 50 to 300mm/min. In contrast, on mild steel in pure nitrogen atmosphere the effect of welding speed is small and nitrogen levels initially increase slightly but then remain constant above speeds of about 100mm/min[13]. A major effect of increasing welding speed (at fixed current) is to decrease the exposed pool area available for nitrogen evolution.

The nitrogen concentration of the weld metal deposited by FCAW (flux cored arc welding) increases with increasing welding voltage, at a rate depending both on the type of electrode and on the nitrogen content of the welding wire[17].

In contrast, the nitrogen concentration of the weld metal decreases as the arc current increases[17]. Higher current involves a higher wire electrode feed rate, which means that more metal per unit time is passing through a given arc volume, causing a shorter reaction time. Therefore, the nitrogen is diluted by additional metal, and decreasing nitrogen level with increasing current is to be expected.

2.2 Metallurgical factors affecting nitrogen absorption

The solubility of nitrogen at one atmosphere in α, γ, δ and liquid iron is shown in Fig.6[18]. The formation of N enhances the dissolution of nitrogen in liquid steel, and the solubility of the nitrogen in the BCC of iron (α and δ) is significantly lower than in the FCC (γ). The equilibrium concentration of nitrogen in liquid iron appears to be 0.04%. As mentioned previously, the solubility in liquid iron is reported to obey Sievert's law, i.e., it is proportional to the square root of the partial pressure.

The solubility of nitrogen in iron is also affected to a great extent by the presence of other elements. The presence of the alloying elements affects the activity coefficient, and hence the solubility of nitrogen in iron. If the alloying element increases the activity coefficient of nitrogen, the solubility of nitrogen will decrease. Solutes having greater affinity for nitrogen than for iron, i.e., where the nitrogen-solute bond energy is greater than the solute-iron or nitrogen-iron bond energies, will generally decrease the activity coefficient, and increase the nitrogen

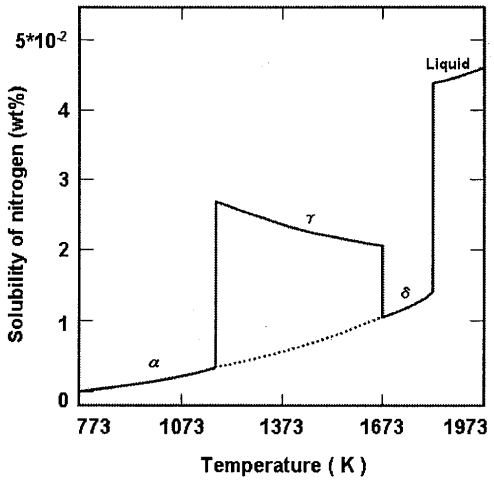

Fig.6 Solubility of nitrogen at one atmosphere in the various modifications of iron as a function of temperature.

solubility. Elements such as Al, Cr, Mn, Mo, Nb, Ta, Ti, V, W and Zr increase the solubility whereas B, C, Co, Cu, Ni, P, Si and Sn decrease the solubility[18-20]. As shown in Fig.7, Ti, Zr, V, Cr, Mn, Mo, Nb, Ta, V and W also increase the solubility whereas C, Ni, and Si decrease the solubility of nitrogen in weld metal of GMA welding[21]. However, the solubility of nitrogen cannot be predicted from the effect of individual alloying elements as there is a synergistic effect exerted between the various alloying elements present. Surface active elements, such as oxygen, sulfur and selenium increase the nitrogen content of the weld metal[22,23].

The review of nitrogen content in stainless steel weld metal resulting from arc welding indicates that the level of nitrogen will depend on welding parameters, compositions of filler metal and base metal, and other metallurgical factors. No consistent trends of behavior were observed and it appears that each individual welding situation has to be evaluated independently.

3. Microstructure of stainless steel weld metal

3.1 Solidification mode

Solidification behavior of stainless steel weld metal can be classified into four modes, A, AF, FA and F, according to their general microstructures and the morphologies of the delta (δ)ferrite, as shown in **Fig.8**[24,25]. In welds of A mode, the weld metal solidifies completely to austenite (γ) and no further transformation takes place during cooling process (Fig.8 (a)). For AF mode, the γ is the leading phase and δ ferrite, if any, solidifies from the rest melt between the cells (Fig.8 (b)). Solidification in FA mode welds is probably the inverse of this, the δ ferrite being the leading phase and austenite solidifying from the rest melt. At lower temperatures the majority of the ferrite is transformed to γ either by an equiaxial or acicular mechanism, depending on the supercooling of δ ferrite (Fig.8 (c)). For F mode, weld metal solidifies completely to δ ferrite and γ is precipitated from the solid ferrite at lower

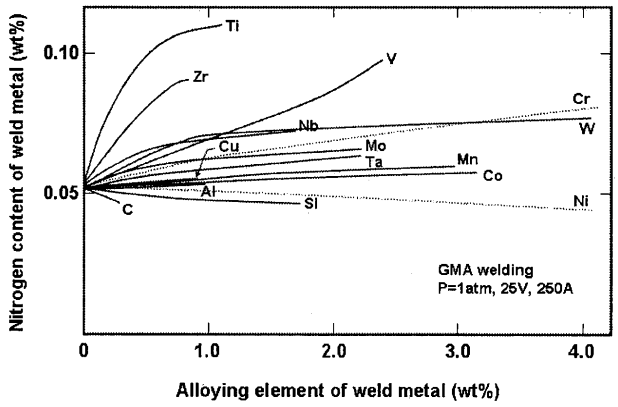

Fig.7 Relation between the alloying element and the nitrogen content of weld metals in a nitrogen welding atmosphere.

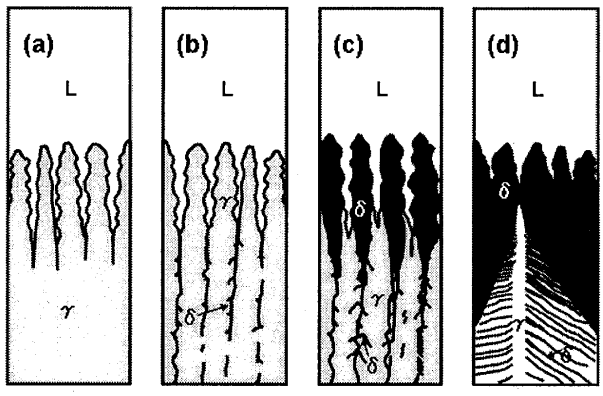

Fig.8 Schematic illustration of solidification model for austenitic-ferritic weld metals:
(a) A mode, (b) AF mode, (c) FA mode,
(d) F mode

temperatures. It nucleates preferentially at the grain boundaries and grows into the interior of the grains by an acicular mechanism as a consequence of pronounced supercooling (Fig.8 (d)). In commercial stainless steel welding alloy, FA mode and AF mode are present in the weld metals of SUS308 and SUS316 series, respectively.

As far as commercial 300-series stainless steels are concerned, solidification modes of weld metals are well described using the chromium (Cr_{eq}) and nickel equivalent (Ni_{eq}). According to Suutala, et al.[26, 27], A, AF, FA and F mode is divided by the ratio Cr_{eq} / Ni_{eq} as follows;

$$F\,\text{mode}: 1.95 \le {Cr_{eq}}/{Ni_{eq}}$$

$$FA\,\text{mode}: 1.48 \le {Cr_{eq}}/{Ni_{eq}} \le 1.95$$

$$A, AF\,\text{mode}: {Cr_{eq}}/{Ni_{eq}} \le 1.14$$

$$Cr_{eq} = [wt\%Cr] + 1.5\times[wt\%Si] + [wt\%Mo] + 0.5\times[wt\%Nb] + 2\times[wt\%Ti]$$

$$Ni_{eq} = [wt\%Ni] + 0.5\times[wt\%Mn] + 30\times[wt\%C]$$

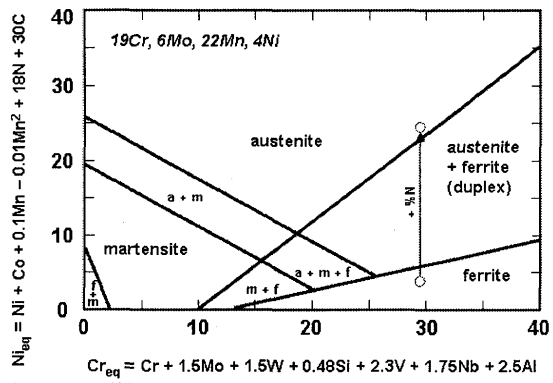

Fig.9 Modified Scheffler diagram for stainless steel weld metal.

Table 2 Various nitrogen coefficients determined in previous studies.

researcher	coefficient of N	N content (wt%)	comment
DeLong [29]	30	0.03~0.22	309, 310, 316, 410
Hull [30]	18.4	0~0.15	309, 308L, 316, 316L
Espy [31]	30(N-0.045) 22(N-0.045) 20(N-0.045)	0.13~0.33	4 nitronic series alloys
Hammer [32]	14.2	0.01~0.20	130 Austenitic S.S
Mel'Kumor [33]	20	0.05~0.46	Austenitic S.S
Okagawa [34]	13.4	0.04~0.29	GTA weld on 304L

These equation note that a higher Cr_{eq} / Ni_{eq} value favors a transition to primary δ ferrite solidification, while the weld metal with a lower Cr_{eq} / Ni_{eq} value will nucleate and solidify as primary γ. Elements such as Cr, Si, Mo, Nb and Ta increase the value of Cr_{eq} / Ni_{eq} whereas Ni, Mn and C decrease the Cr_{eq} / Ni_{eq} value.

On the other hand, it has been recognized that nitrogen behaves as an austenizer in the weld metal. **Fig.9** shows the highly austenite-forming character of the nitrogen by the way of a modified Schaeffler diagram[28]. Through the addition of 1%N, a purely ferritic stainless steel is rendered completely austenitic. But, as for the weld metal containing a higher amount of nitrogen and or manganese, such description and prediction were found to be inaccurate, and other suitable expressions or equivalents for them have been sought and developed, as shown in **Table 2**[29-34]. Suutala, et al., stated that the solidification mode of austenitic stainless steel weld metal containing up to 0.23% nitrogen can be described using Hammer's equivalents. In contrast, Okagawa, et al., reported that in nitrogen-added type 304 welds, the nitrogen effect on ferritic content was smaller than that predicted by DeLong, and they estimated the nitrogen coefficient for the nickel equivalent expression as 13.4, which was considerably lower than the coefficient of 30 determined by DeLong. Espy reported that the nitrogen effect as an austenizer decreased as the nitrogen content increased, and proposed the modified Schaeffler diagram, in which the nitrogen coefficient varied from 30 to 20 with

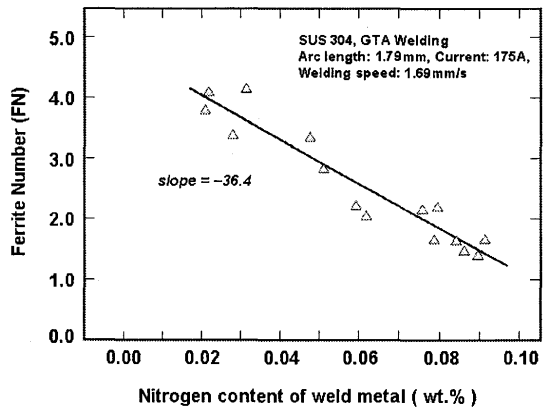

Fig.10 Ferrite number as a function of weld metal nitrogen content.

nitrogen content. The discrepancies in the nitrogen effect result in a serious drawback in developing proper weld compositions that confer the desired ferrite content and distribution. Hence, more systematic work is necessary to verify the nitrogen effects on solidification behavior of stainless steel welds.

3.2 Ferrite number

In many applications, the ability to control the δ ferrite content of stainless steel weld metal is important to balance hot cracking resistance, corrosion resistance and fracture toughness. Whereas "percent ferrite" has been used as an indicator of ferrite measurement for decades, it has become an uncertain value with large errors because of the lack of reference standards or agreement on calibration procedure. As a result, the index of measurement is chosen as a magnetic attraction scale expressing ferrite contents in weld metals as a ferrite number (FN).

The delong diagram considering the effect of nitrogen is probably the most popular method for predicting the ferrite content of stainless steel weld metals. A position on the diagram is determined from the composition and then related to a series of ISO-FN lines[35]. Good agreement has also been obtained in the study of shielded metal arc welds. However, the Delong diagram developed for low nitrogen containing austenitic stainless steels is not suitable for the higher manganese, higher nitrogen grades. For example, manganese content beyond 4wt% is not potent as an austenite stabilizer, and may in fact act as a ferrite former.

A significant portion of the efforts in evaluating the influence of nitrogen in stainless steel weld metals has been devoted to the evaluation of it's influence on the δ ferrite content. In almost all the literature examined, regardless of welding process, the increase of nitrogen in the weld metal has resulted in a decrease in the δ ferrite content. As shown in **Fig.10**[34], the nitrogen austenite stabilization is apparent by a significant decrease in δ ferrite content (FN) with an increase in weld metal nitrogen.

On the other hand, in an extensive examination of the

ferritic content of 308, 316, 310 and duplex stainless steel weld metals containing high nitrogen and manganese levels, McCowan, et al.[36], proposed a predictive equation of the following type:

$$FN1 = -15.2 + 2.2[Cr + Mo + 0.5(Si) + 15(Ti) + 0.8(Nb)] - 1.9[Ni + 17(N) + 30(C)]$$

In addition, for stainless steel weld metals with FN>1, the predictive equation of FN is given by:

$$FN = -18 + 2.9[Cr + Mo + 0.3(Si)] - 2.6[Ni + 20(N) + 36(C) + 0.3Mn]$$

Although the coefficient of nitrogen is different among researchers, the δ ferrite content (FN) in stainless steel weld metals depends strongly on the chemical composition of the stainless steel, especially its nitrogen content.

4. Weld defects

4.1 Blowhole

One of the problems encountered in the welding of HNS is porosity. Porosity in welds is caused by gas entrapment in the molten metal, by too much moisture on the base or filler metal, or by improper cleaning of the joint during welding preparation.

The cause of porosity in HNS weld metal is attributed to nitrogen gas that is escapes as porosity due to a difference in nitrogen gas solubility between molten and solid metals. Another possibility is that nitrogen gas is generated by some type of rapid reaction and is trapped in the weld metal.

In the HNS (304 Stainless steel), for example, nitrogen levels near the upper limit of 0.35% can result in porosity in GTA weld deposits, whereas lower levels (above approximately 0.25%) can result in excessive porosity in electron-beam welds[30]. Furthermore, the critical nitrogen content is dependent on the welding parameters, especially arc length. If the arc length increases, the nitrogen solubility in the molten pool will increase, and will prevent of porosity. Morigaki, et al., reported that porosity was generated when the nitrogen level in submerged-arc weld metals exceeded 230ppm for ferritic steel.

Ogawa, et al.[38], stated that extensive porosity occurred in the weld bead on 304 stainless steel, but there was absolutely no sign of such an occurrence with 310S stainless steel which contains a relatively large amount of chromium. As was mentioned in Section 2.2, elements such as Ti, Zr, Nb, V, Cr, Mo and Mn increase the solubility of nitrogen in the weld metal, while C, Si and Ni decrease it. Hence, the porosity occurring through the use of a large amount of nitrogen near the solubility limit can be remedied by an appropriate increase in, or by the addition of such solubility-increasing elements. Okuda[39] also reported on the porosity generation during the submerged-arc welding of Y-groove. He showed that it was effective for the prevention of porosity to add nitrogen-fixing elements. Hirabayashi, et al.[40], demonstrated the same method of porosity prevention by

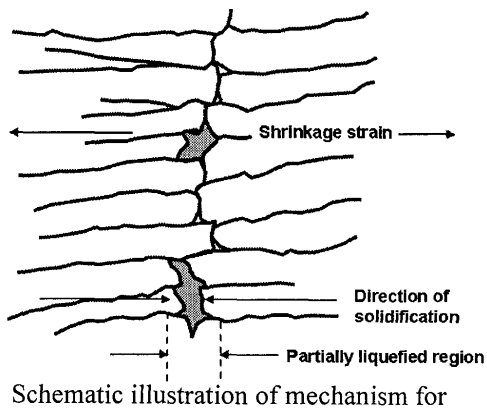

Fig.11 Schematic illustration of mechanism for solidification cracking.

adding Ti and Zr. They have also reported that porosity in the weld metal can be prevented by adding a small amount of oxygen gas to the argon shielding gas. However, for GTA welding with oxygen gas, electrode erosion results in excessive sputtering and arc instability.

On the other hand, porosity can occur as a result of surface contamination, such as by oil and greases or undetected leaks in water-cooled welding torches or weld fixtures. Thus, surface should be thoroughly cleaned prior to welding.

4.2 Weld cracking

(1) Solidification cracking

The two most serious problems encountered in the welding of high nitrogen containing stainless steels are solidification cracking in weld metal and liquation cracking in heat-affected zone (HAZ).

Solidification cracking, which results from the non-formation of low-melting liquid films along grain boundaries to accommodate the thermal shrinkage strains associated with the last stages of solidification, as shown in **Fig.11**. Hence, solidification cracking susceptibility is dependent on the amount of residual liquid phases and thermal strain occurring in interdendritic regions. This susceptibility is increased by elements that promote the formation of liquid phases in grain boundaries. These elements include sulfur and phosphorus, which are often present as impurities, and Si, Nb, Ti, and B, which are sometimes present as minor alloying additions.

On the other hand, solidification modes of weld metal can have a profound influence on the occurrence of solidification cracking. Cracking susceptibility is drastically reduced in welds that solidify as primary ferrite with the peritectic or eutectic solidification of austenite (FA mode), even at high levels of phosphorus and sulfur[41]. The formation of the grain boundary in the FA mode may promote a scavenging effect for a large percentage of the grain boundary segregates, in particular, sulfur. Sulfur, having higher solubility in δ ferrite than in austenite, might preferentially separate to the ferrite, thus starving the grain boundary of sulfur. This may reduce the likehood of liquid film formation caused by suppression of the solidus along the grain boundary, in turn reducing the solidification cracking tendency.

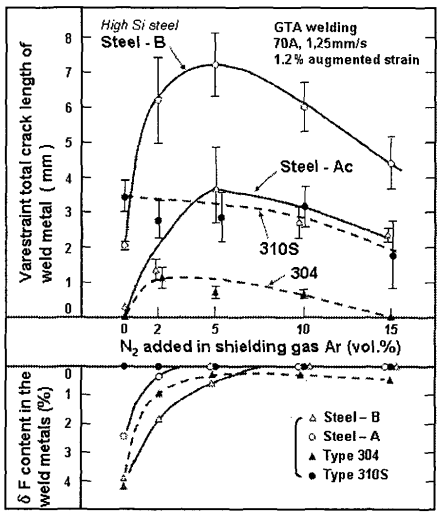

Fig.12 Influence of nitrogen in shielding gas on the hot cracking susceptibility of austenitic stainless steel weld metal.

In addition, the grain boundary ferrite may play a significant role in altering the interfacial energy considerations, as follows. In the presence of grain boundary ferrite, since the γ - δ boundary interfacial tension is lower than γ - γ boundary tension, based on the interfacial energies considerations, liquid films may not be penetrating deep into the grain boundaries and so reduce the propensity for solidification cracking.

Since the amount of δ -ferrite in the weld metal is decreased by nitrogen addition, high nitrogen containing austenitic stainless steel may be susceptible to solidification cracking. Nishimoto, et al. [42], reported that the nitrogen addition and the primary austenite solidification do not improve the solidification cracking susceptibility of SUS304 laser weld. Similar figures are also given by Mastuda, et al. [43], and Brooks[44]. However, Lundin, et al. [45, 46], did not detect any increase in the solidification cracking susceptibility with increasing nitrogen and decreasing ferrite, probably because of the low levels of sulfur and phosphorus in their steels. Furthermore, Ogawa, et al.[41], demonstrated an increase in solidification cracking resistance of fully austenitic SUS310 weld metal with nitrogen added to the argon shielding gas (see **Fig.12**).

(2) Liquation cracking

Liquation cracks are defects that can occur during fusion welding in either the HAZ in the base material or in previously deposited weld metal reheated by subsequent welding. This form of cracking is always intergranular and located immediately adjacent to the fusion boundary. In many applications it is probable that liquation cracks have no detrimental effects on service performance, since the cracks are so small and often sub-surface; however, in certain circumstances they may contribute to premature failure.

The mechanisms proposed for liquation cracking in particular have been reviewed by a number of researchers. However, a generalized schematic representation as

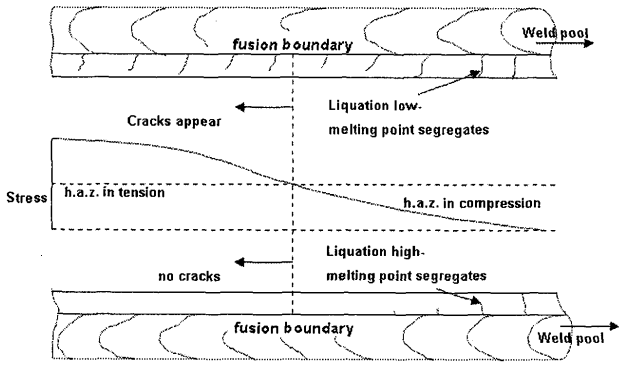

Fig.13 Schematic illustration of the mechanism by which tensile stresses in the HAZ, combined with relatively long-lived liquated films, produce cracking.

regards liquation cracking is shown in **Fig.13**, after Puzak, et al[47]. During the initial passage of the molten pool, the HAZ is in compression, and the presence of intergranular-liquated films at this stage will not result in cracking. As the weld pool advances beyond a particular point, contraction stresses from cooling eventually result in tensile strains in the HAZ and if liquid films are present at this stage, cracking may occur. It may thus be seen that, other things being equal, the lower the melting point of an intergranular film below that of the bulk solidus the greater will be the potential extent of liquation cracking.

In many studies examining the liquation cracking behavior of austenitic stainless steels, the presence of sulfur and phosphorus has been identified with increased liquation cracking susceptibility in HAZ[48-55]. To a somewhat lesser extent, so have Si and Nb. The presence of Si in amounts greater than 0.3% leads to a rapid increase in susceptibility to liquation cracking. Ti and Nb influence on liquation cracking susceptibility is generally detrimental. Each of these elements appears to increase cracking susceptibility in two possible ways. The first is by promoting the formation of low melting-point constituents, and the second is by acting as a surfactant which promotes wetting of solidifying grain boundaries.

On the other hand, very little information is available on the nitrogen dependence of liquation cracking susceptibility. Long, et al.[56], reported that dissolved nitrogen in the weld metal can be significantly influence by welding variables and, under certain conditions, can reduce the amount of δ ferrite in a reheated weld metal microstructure below that adequate to prevent liquation cracking. In contrast, Woo, et al.[57], demonstrated that the nitrogen addition could improve liquation cracking susceptibility of austenitic stainless steel welds due to the effect of nitrogen in suppressing grain growth in HAZ. Smaller grain size reduces liquation cracking, perhaps primarily by increasing grain boundary area/unit volume.

The foregoing results suggest that the effect of nitrogen on the hot cracking, i.e., solidification cracking in weld metal or liquation cracking in HAZ of fully austenitic welds is controversial, and further study is necessary.

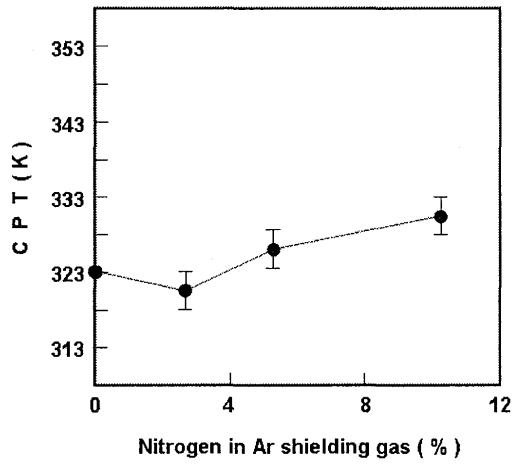

Fig.14 Effect of nitrogen content of the shielding gas on CPT of welds measured by $FeCl_3$ immersion test according to ASTM G48-76.

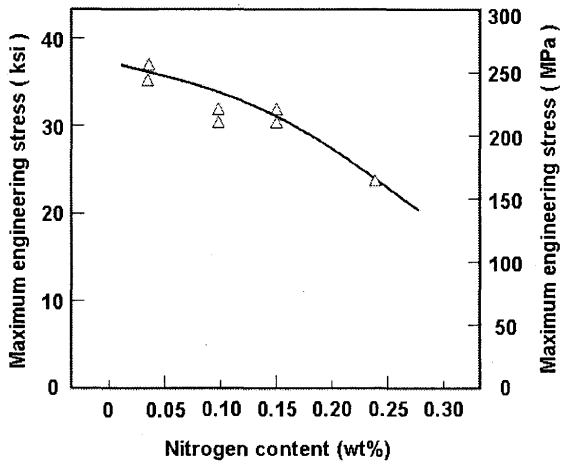

Fig.15 Maximum engineering stress vs. wt% nitrogen for type 304 weld metal specimens tested in boiling $MgCl_2$.

5. Corrosion properties

It has long been known that nitrogen has an effect on the improvement of corrosion properties, such as pitting corrosion resistance, crevice corrosion resistance and stress corrosion cracking (SCC). The effect of nitrogen in pitting corrosion resistance can be explained by the following considerations: Nitrogen dissolves during the corrosion reaction to form the ammonia ion, NH_4^+, at pit sites and results in the pit electrolyte being less acidic by increasing the pH. Nitrogen is also enriched at the surface while other metals preferentially dissolve, and improved the passivity. Nitrogen dissolves to form stable Cr-nitrides which might act as inhibitors locally at the pit sites. Nitrogen has a markedly decelerating effect on $M_{23}C_6$ and χ phase precipitation and on σ phase precipitation.

Limited information is available in the literature on the effects of nitrogen on the corrosion properties of austenitic stainless steel welds and these are described below. **Fig.14** shows effect of nitrogen content of the shielding gas on critical pitting corrosion temperature (CPT) of super austenitic stainless steel GTA welds[58]. The results indicate that the CPT values of weld metal increase with increasing weld nitrogen content through the shielding gas. Similar results are also given by Hertzman, et al.[59], and Ogawa, et al.[60]. They have reported a vast improvement in the pitting corrosion resistance of nitrogen containing GTA weld metals. In addition, Ogawa, et al.[61] demonstrate that for utilizing the effect of nitrogen on pitting corrosion resistance of weld metal, it is effective to change the composition and enhance the nitrogen solubility of weld metal by adding elements, such as Mn, to the filler metal. Cieslack, et al.[62], report similar results with GTA welding of SUS304 stainless steel. An addition of 0.2% nitrogen was found to increase the pitting potential of weld metal by two times as compared to no nitrogen. Pitting was found to initiate at the δ -ferrite/austenite interface, and thus the addition of nitrogen reduces the available δ -ferrite/austenite interface for possible occurrence of pitting. According to Mudali, et al.[63], the relationship between the critical pitting potential (E_{pp}) and nitrogen content was given by:

$$E_{pp} = 0.175[\underline{N}] + 140$$

Where E_{pp} is in millivolts and the nitrogen content [N] is in ppm.

Nitrogen has also been reported to improve the crevice corrosion characteristics of austenitic stainless steel weld metal. Kearns[64] notes that the nitrogen addition raised the critical crevice corrosion temperature of 20Cr-25Ni-6Mo steel autogenously welded strips from 305K to that of the base metal (310.5K). Garner[65] also reports the improvement in the crevice corrosion resistance of SUS 316 weld metal with increasing nitrogen contents.

On the other hand, nitrogen is reported to decrease resistance to stress corrosion cracking (SCC) of austenitic stainless weld metal. Baeslack, et al.[66], found that the addition of nitrogen to welds of SUS 304 stainless steel decreased the resistance to SCC in $MgCl_2$ (see **Fig.15**). This is associated with the decrease in ferrite amount with increasing nitrogen contents, with fully austenitic weld metals being highly susceptible to SCC. The increased susceptibility of the fully austenitic weld metal is probably promoted by the large grain size and the presence of smooth, ferrite-free grain boundaries. Namely, crack propagation is aided by coarse-grained austenite which results from the lack of a pinning effect since no residual ferrite is present.

6. Mechanical properties

6.1 Tensile properties

The effects of nitrogen on the tensile properties of austenitic stainless steel welds can be listed as follows: (1) effect as a nitrogen solute, and (2) effect as a nitride.

Nitrogen was more effective in improving the tensile strength at lower temperatures than at room temperature. Enjo, et al.[67], have conducted extensive research on the mechanical properties of SUS316 GMA welds containing nitrogen. Their results shown in **Fig.16** indicate that the tensile strength of weld metal has around 75kg/mm^2 at

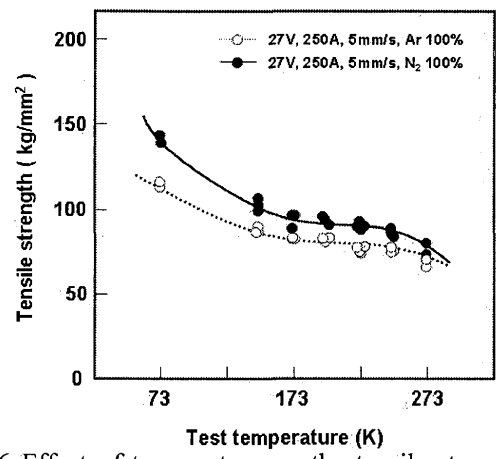

Fig.16 Effect of temperature on the tensile strength of SUS 316 welds made in N_2 shielding gas.

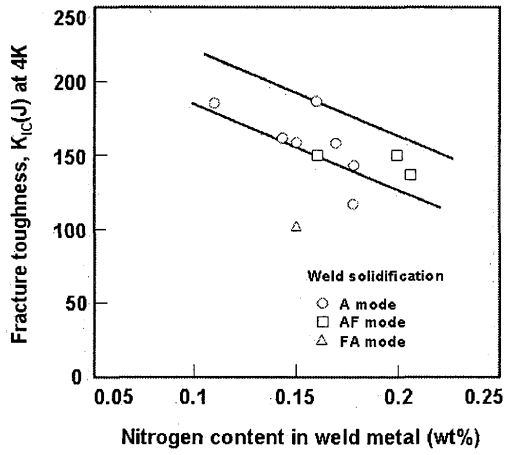

Fig.17 Effects of nitrogen content and solidification mode on the fracture toughness, $K_{IC}(J)$, of the GTA welds at 4K.

0℃, and 145kg/mm^2 at –196℃, respectively. Similar results for 316L weld metals are reported by other researchers, too. Ogawa, et al.[68], report that the strengthening effect of nitrogen at 4K was remarkable, and a 0.1wt% increase in nitrogen content led to an increase of yield strength by approximately 300MPa at 4K, which was nearly 1.5 times greater than that at 77K. Mccowan, et al.[69], also notes that increasing the nitrogen content from 0.05 to 0.25wt% linearly increased the 4K yield strength from 600 to 1300MPa. The equation relating the yield strength to the nitrogen content was:

$$\sigma_Y = 400 + 3700(wt\%N)$$

Where σ_Y is weld yield strength (MPa at 4K) and the wt%N is nitrogen content.

The mechanism of strengthening due to nitrogen solute can be mainly attributed to lowering of the stacking fault energy and thus increasing the tensile or yield strength.

Although the solubility of nitrogen is greater than the solubility of carbon, high nitrogen containing austenitic stainless steels are susceptible to nitride precipitation during welding or heat treatment[70-72]. The presence of nitrides has been shown to be detrimental to the mechanical properties of high nitrogen containing austenitic stainless steels, however, no systematic study has been conducted in the past. Woo, et al.[71], report that the tensile strength of the friction welds decreased with increasing friction time or low nitrogen containing-material. They also demonstrate that the reduction of tensile strength with increasing friction time or low nitrogen containing-material could be due to an increase in intergranular Cr-nitride precipitates. The detrimental effect of Cr-nitrides on the tensile property of a friction weld is generally explained by a mechanism as follows. It is recognized that nitrogen is a strengthening alloy addition through its action as an interstitial solid solution strengthener. Therefore, an increase in the quantity of intergranular Cr-nitrides during friction welding reduces the nitrogen content in the matrix, which seems to be responsible for lower tensile properties of the joint due to a reduction of solid solution strengthening-effects.

6.2 Impact toughness

Metallurgical factors such as δ ferrite, and alloying elements such as N, O, C have been found to be the dominant factors in determining toughness of austenitic stainless steel welds. Higher ferrite number (FN) tends to decrease the toughness of welds. Szumachowski, et al.[73,74], reported that toughness of austenitic stainless steel weld metals varied inversely with decreased ferrite content. Furthermore, they also demonstrate that maximum toughness at cryogenic temperatures can be obtained using fully austenitic weld metals. Similar results are reported by other researchers, also.

On the other hand, increased nitrogen content, which lower the FN, have been reported to lower the toughness of welds. As far as the influence of nitrogen on the toughness of austenitic weld metals is concerned, Ogawa, et al.[68], reported that increased nitrogen content loaered the weld fracture toughness at 4k (see **Fig.17**). This diagram also shows that the weld in the FA solidification mode exhibits the lowest fracture toughness, despite the medium nitrogen content in the range of interest. Szumachowski, et al.[74], in their evaluations of type 316 SMA weld metals, indicate a decrease in toughness with increasing nitrogen between –129℃ and –196℃. As mentioned in earlier, nitrogen is generally believed to reduce toughness, whereas Enjo, et al.[75], report an increase in toughness with increasing nitrogen at –50℃ as well as 400℃ for type 304 weld metal. However, no discussion of ferrite contents was given. These differences and the variations in toughness values indicate that the role of nitrogen with respect to toughness requires further study.

Compared with weld metals, very little information is available on the nitrogen dependence of toughness properties in HAZ. The presence of nitrides has been shown to be detrimental to the toughness properties of austenitic stainless steel welds. Simmons, et al.[70], attributed the reduced fracture toughness of high nitrogen containing stainless steels to the presence of nitrides in

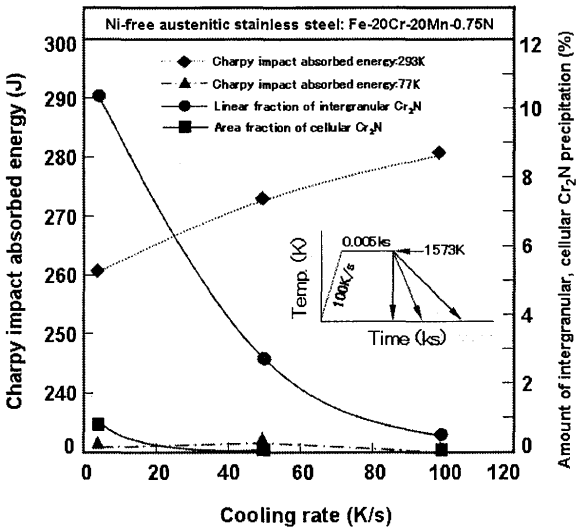

Fig.18 Effect of cooling rate on Charpy impact absorbed energy and amount of intergranular, cellular Cr_2N precipitation.

samples aged at temperature between 600℃ and 900℃. Kikuchi, et al.[9], also reported that toughness of weld metal increases in case of less than 4000ppm nitrogen content, whereas if nitrogen content exceeds 4000ppm, Cr_2N precipitates are formed at grain boundaries, and toughness of weld metal decreases. As shown in **Fig.18**, Woo, et al.[76], noted that intergranular and cellular Cr_2N precipitation reduced the impact property of the HAZ at room temperature. In addition, they also noted that embrittlement occurred due to grain boundary separation and fracture through cellular precipitation regions, initiated at Cr_2N.

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