Title	Solidification Crack Susceptibility in Weld Metals of Fully Austenitic Stainless Steels (Report VII) : Effect of Mn and N on Solidification Crack Resistance(Materials, Metallurgy & Weldability)
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Citation	Transactions of JWRI. 1982, 11(2), p. 79-85
Version Type	VoR
URL	https://doi.org/10.18910/7004
rights	
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Solidification Crack Susceptibility in Weld Metals of Fully Austenitic Stainless Steels (Report VIII)†

— Effect of Mn and N on Solidification Crack Resistance—

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Abstract

The effects of Mn and N on the cracking susceptibility of SUS (AISI) 310S fully austenitic stainless steel weld metals were investigated by making the Trans-Varestraint test and other hot cracking tests. The beneficial effect of Mn in reducing cracking was confirmed, and it was revealed that its degree was greater as the S content was larger. For commercial SUS310S (0.02-0.03%P, 0.003-0.02%S) the optimum Mn content was about 3 to 6% according to the S content. The metallurgically beneficial effect of Mn was attributed to the reduction in the deleterious effect of S. It was also found that N had a neutral effect or a slightly detrimental effect on the cracking resistance of commercial SUS310S weld metals.

KEY WORDS: (Austenitic Stainless Steels) (Weld Metals) (Hot Cracking) (Weldability Tests) (Manganese) (Nitrogen)

1. Introduction

In recent years there has been an increasing need for fully austenitic stainless steels for many uses in chemical plants, power stations and nuclear reactors. However, it has been known for many years that fully austenitic weld metals are subject to solidification cracking[1),2)]. For this reason, a number of researchers investigated the causes and the mechanism of cracking and the compositional remedy to improve cracking susceptibility[3)–14)].

Concerning the compositional modification, Hull[3)], Gueussier and Castro[4)], and Borland and Younger[1)] showed that the addition of Mn to fully austenitic stainless steels has a favourable effect and Gooch and Honeycombe[6)] recommended that the presence of between 4 and 6 % Mn was the most beneficial and also N should be increased up to 0.2%.

A series of metallurgical work has similarly been carried out at the JWRI[8)–14)] with the objective of producing crack-resistant, fully austenitic weld metals. As a result it was pointed out[12),13)] that a decrease in each of the P and S content to 0.005% and less was extremely beneficial in preventing or minimizing cracking in practical welds of fully austenitic stainless steels. From the result of the statistical analysis of the brittleness temperature range(BTR) it could be seen that Mn and N might exert a little favourable effect[13)]. Moreover, in the previous paper[14)], for commercially available SUS310S containing about 0.02 to 0.03%P, it was revealed that the optimum content of La or REM addition according to the P and S content had a greatly beneficial effect on the improvement of cracking resistance. Also, for SUS310S containing about 0.03%P and 0.05%S, the addition of about 6%Mn was shown to be effective in reducing the BTR, or the cracking susceptibility[14)]. However, as described previously[9)], the addition of Mn(1 to 7%) to SUS310S containing 0.023%P and 0.003%S caused little or no change in the BTR and the ductility curves. From these results it is naturally understood that the effect of Mn is chiefly related to the S content.

Therefore, the present work was undertaken to establish firmly the effect of Mn on cracking susceptibility in fully austenitic weld metal on the basis of a study of the interrelated effects of Mn and S or P. The Mn content was varied from 1 to 7% in SUS310S type 25%Cr–20%Ni alloys containing different combinations of the P and S contents. These materials were first subjected to the Trans-Varestraint test, and then the results were confirmed by other practical hot cracking tests. The influence of Mn on the liquidus and the solidus temperature and the formation numbers of phosphides and sulphides were investigated by using thermal analysis method with crucible and the energy dispersive x-ray spectoanalysis (EDX) method of the scanning electron microscope, respectively. Besides, since N is liable to incursion from the atmosphere and the beneficial effect of N has been reported as

† Received on September 30, 1982

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Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka, Japan

mentioned above[6),9)], the effect of N on cracking susceptibility was examined by using the Trans-Varestraint test and GTA spot welding crack test.

2. Materials and Experimental Procedure

2.1 Materials used

Several Mn contents were made to fully austenitic materials containing 8 different combinations of the P and S contents in the range of about 0.002 to 0.025% and 0.002 to 0.05%, respectively, based on the SUS310S specification. These chemical compositions are given in **Table 1**. The compositional levels of Group Ⅱ, Ⅲ and Ⅳ correspond to those of commercially available SUS310S. The details of such production are the same as those in the previous report[14)]. Furthermore, the materials close to the chemical compositions of Group Ⅳ and Ⅷ were particularly obtained to confirm the effect of Mn in the case of low S content. They are given in Group Ⅰ and Ⅱ of **Table 2**.

Table 1 Chemical compositions of SUS310S containing various combinations of P and S content with several contents of Mn added intentionally.

Group	Material, Element	Composition (wt%)
Ⅰ	310S-Ⅰ	0.08C-0.97Si-1.21Mn-0.028P-0.05S-24.38Cr-19.94Ni
	Mn	(1) 2.22 (2) 3.23 (3) 4.94 (4) 6.45
Ⅱ	310S-Ⅱ	0.06C-0.68Si-1.1Mn-0.025P-0.015S-24.5Cr-19.5Ni
	Mn	(1) 2.88 (2) 5.71
Ⅲ	310S-Ⅲ	0.06C-0.6Si-1.06Mn-0.025P-0.007S-24.5Cr-19.5Ni
	Mn	(1) 3.21 (2) 6.08
Ⅳ	310S-Ⅳ	0.05C-0.5Si-1.0Mn-0.024P-0.002S-24.6Cr-19.3Ni
	Mn	(1) 3.25 (2) 6.24
Ⅴ	310S-Ⅴ	0.06C-0.7Si-1.46Mn-0.11P-0.007S-25.0Cr-19.5Ni
	Mn	(1) 2.90 (2) 6.22
Ⅵ	310S-Ⅵ	0.05C-0.6Si-1.05Mn-0.014P-0.003S-24.5Cr-19.5Ni
	Mn	(1) 3.86 (2) 6.03
Ⅶ	310S-Ⅶ	0.07C-0.7Si-1.76Mn-0.002P-0.007S-25.3Cr-19.5Ni
	Mn	(1) 3.40 (2) 6.95
Ⅷ	310S-Ⅷ	0.06C-0.6Si-1.08Mn-0.002P-0.004S-24.5Cr-19.5Ni
	Mn	(1) 2.73 (2) 4.86 (3) 6.92

Table 2 Chemical compositions of SUS310S containing very low S content and commercial level (Ⅰ) and very low level (Ⅱ) of P with various contents of Mn added intentionally.

Group	Material (SUS)	Composition (wt%)						
		C	Si	Mn	P	S	Cr	Ni
Ⅰ	310S-Mn1	0.063	0.69	1.15	0.023	0.003	24.60	20.20
	310S-Mn2	0.065	0.70	1.90	0.022	0.003	25.15	19.90
	310S-Mn3	0.065	0.70	2.75	0.022	0.003	24.90	19.90
	310S-Mn4	0.063	0.68	4.70	0.019	0.005	24.55	19.50
	310S-Mn5	0.063	0.65	6.20	0.021	0.004	24.20	19.30
Ⅱ	310S-M1	0.06	0.55	0.97	0.001	0.003	24.62	19.52
	310S-M2	0.07	0.51	2.90	0.001	0.004	24.67	19.77
	310S-M3	0.06	0.60	4.68	0.001	0.005	25.19	20.23
	310S-M4	0.06	0.56	7.10	0.001	0.006	24.44	19.94

Table 3 Chemical compositions of commercial SUS310S used to study effect of N.

Material (SUS)	Composition (wt%)						
	C	Si	Mn	P	S	Cr	Ni
310S	0.07	0.61	1.69	0.017	0.002	25.02	19.16

The effect of N content was investigated by using weld metals made in Ar—5%N_2 or Ar—20%N_2 shielding gas instead of Ar gas during GTA welding. The composition of the base SUS310S is shown in **Table 3** and the contents in weld metals were approximately 0.03, 0.095 and 0.165% for Ar, Ar—5%N_2 and Ar—20%N_2 shielding atmosphere, respectively.

2.2 Hot cracking test

The Trans-Varestraint test[15)], which was found to be a useful test for assessing cracking susceptibility by determining the BTR and the ductility curve[13),14)], was conducted on the plates of 5mm thickness in Table 1 and of 3mm thickness in Table 2, when GTAW was performed under the conditions of 150A, 15V and 100mm/min and 100A, 12.5V and 150mm/min, respectively. The details of all testing procedures and their index of cracking susceptibility were described in the previous reports[9),14)]. For 3mm thick rolled-plates of Group Ⅱ of Table 2, the Show-Bending Speed type Trans-Varestraint test[10)] was utilized to define the effect of Mn on cracking tendency in the case of very low P and S content. Moreover, in order that the susceptibility of practical production welds to solidification cracking could be assessed, each material was subjected to the modified CPT(cast pin tear) test[14)], GTA bead-on-plate welding under the parameters of 250A, 20V and 1400mm/min for 5mm thick plates and 350A, 20V and 1000mm/min for 20mm thick plates[14)], GTA spot welding under 300A, 20V and 2sec[14)], EB bead-on-plate welding under 15mA, 150kV, 2000mm/min and a_b=1.0[13),14)], and/or resistance spot welding under 700kg, 12kA and 15c/s, and 1400kg, 17kA and 20c/s[12)].

3. Results and Discussion

3.1 Effect of Mn on cracking susceptibility of SUS310S

3.1.1 Effect of Mn on BTR

Figure 1 shows the relationship between the BTR at an augmented strain of about 4% and Mn content for each level of P and S content in weld metals. As established in the previous reports[12),13)], the BTR for about 1 to 1.5%Mn narrowed with a decrease in P and S content. In the case of Ⓘ 0.028%P and 0.05%S, as described in the previous report[14)], the BTR was remarkably decreased from 320 to 225°C according to an increase in Mn content from about 1 to 6.5%. The BTR for Ⓘ 0.025%P and 0.015%S and Ⓘ 0.025%P and 0.007%S was narrowed by around 25 and 15°C, respectively, with the addition of about 6%Mn. Howev-

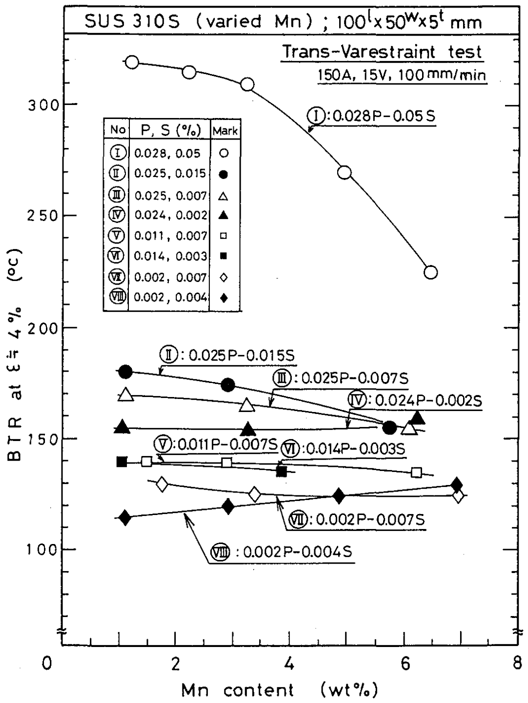

Fig.1 Effect of Mn content on BTR at $\varepsilon \fallingdotseq 4\%$ for SUS310S containing various combinations of P and S content.

er, in the case of (IV) 0.024%P–0.002%S, (V) 0.011%P–0.007%S, (VI) 0.014%P–0.003%S and (VII) 0.002%P–0.007%S, the BTR showed no or small variations in the range of about 1 to 6.5%Mn, but on the contrary in the case of (VIII) 0.002%P and 0.004%S the BTR showed a tendency to be broadened with an increase in Mn content.

Subsequently, to confirm further the effect of Mn for very low S content, the Trans-Varestraint test and/or the SB Trans-Varestraint test were conducted on the materials of Table 2. The results are given in **Table 4** and **Fig.2.** In the case of 0.023%P and 0.003%S, according to Group I in Table 4, the CST value[9] appeared to increase in a degree although the BTR at a large augmented strain increased very slightly with Mn addition. Furthermore, the SEM observation result of solidification crack surface in the Trans-Varestrant test specimens indicated that the temperature ranges of Type D and Type D–F crack surface[11] over which cracking would be liable to initiate were narrower at about 4 to 6%Mn. It is therefore judged that the Mn addition might be rather detrimental or neutral to reduction in cracking under greater applied-strain conditions but slightly beneficial under smaller strain conditions which is considered to be more common in practical production welding. In the case of about 0.001%P and 0.004%S, from Group II in Table 4 and Fig.2 it was seen that with an increase in Mn conent the BTR and the area

Table 4 BTR and CST obtained by Trans-Varestraint test for SUS310S containing various Mn contents for (I) commercial and (II) very low levels of P.

Group	Material (SUS)	Mn (wt%)	BTR(°C) at ε=2.5%	CST(%/°C) (x10^{-3})
I	310S-Mn1	1.15	155	1.15
	310S-Mn2	1.90	160	1.15
	310S-Mn3	2.75	160	1.20
	310S-Mn4	4.70	160	1.25
	310S-Mn5	6.20	160	1.25
II	310S-M1	0.97	100	3.9
	310S-M2	2.90	110	3.4
	310S-M3	4.68	115	3.0
	310S-M4	7.10	125	2.4

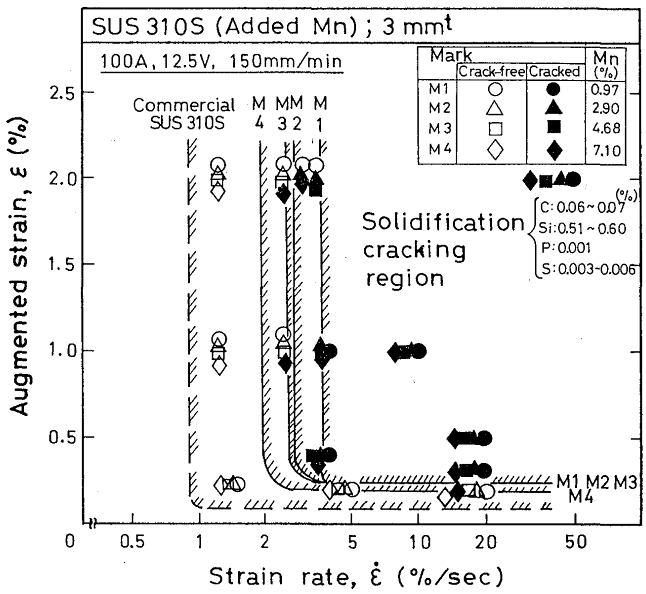

Fig.2 Effect of Mn content on conditions of augmented strains and strain rates required to cause cracking in SUS310S containing very low contents of P and S.

showing the conditions of augmented-strains and strain rates required to cause cracking broadened and the CST value decreased; however, the area for 6.4%Mn was even narrower than that of commercial SUS310S. It is consequently considered that the Mn addition would not be effective in reducing cracking for weld metals containing very low P and S, yet the cracking resistance at 6%Mn would be much greater than that of commercial SUS310S.

Judging from the above results, it was in the case of higher S content that the Mn addition enabled the BTR to narrow, and the higher the S content was, the more effective the Mn addition was. On the other hand, it appeared that in the case of extremely low S content the Mn addition had little effect on a reduction in the BTR and the Mn addition might exert a harmful effect on cracking susceptibility as the case might be, for example, when the P and S content were very low and applied strains were large.

3.1.2 Effect of Mn on cracking susceptibility

To confirm further the effect of Mn, the modified CPT test and GTA spot and bead welding crack test were conducted on all the materials in Table 1, and these results are summarily shown in **Fig.3.** It shows the relationship between Mn content and cracking susceptibility separately at each combination of P and S. According to the modified CPT test results, cracking ratio, C_R, decreased with a decrease in P and S content, and except for very low P and S content C_R was further decreased with Mn addition. The reduced degrees of C_R were more remarkable in the case of higher S content and such tendencies were almost the same as those of the BTR. GTA spot and bead welding test show that cracks were observed at about 1%Mn in weld metals of only commercial materials with 0.024–0.025%P and 0.002–0.015%S but not at about 3 to 6% for about 0.025%P and 0.002 to 0.007%S and at approximately 6%Mn for 0.025%P and 0.015%S. As a result, the addition of Mn was confirmed to be beneficial in reducing cracking in weld metals of commercial SUS310S. **Figure 4** shows the relation between cracking susceptibility(total crack length, L_T) in GTA bead and resistance spot welding crack test and Mn content for weld metals containing about 0.023%P and 0.003%S in Graup I of Table 2. Crack-

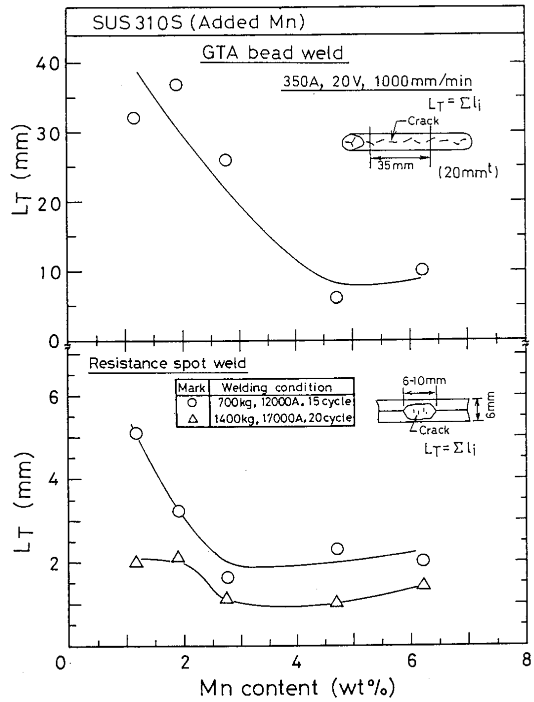

Fig.4 Results of GTA bead welding and resistance spot welding showing effect of Mn content on cracking susceptibility (amount of cracking) of SUS310S containing about 0.023%P and 0.003%S.

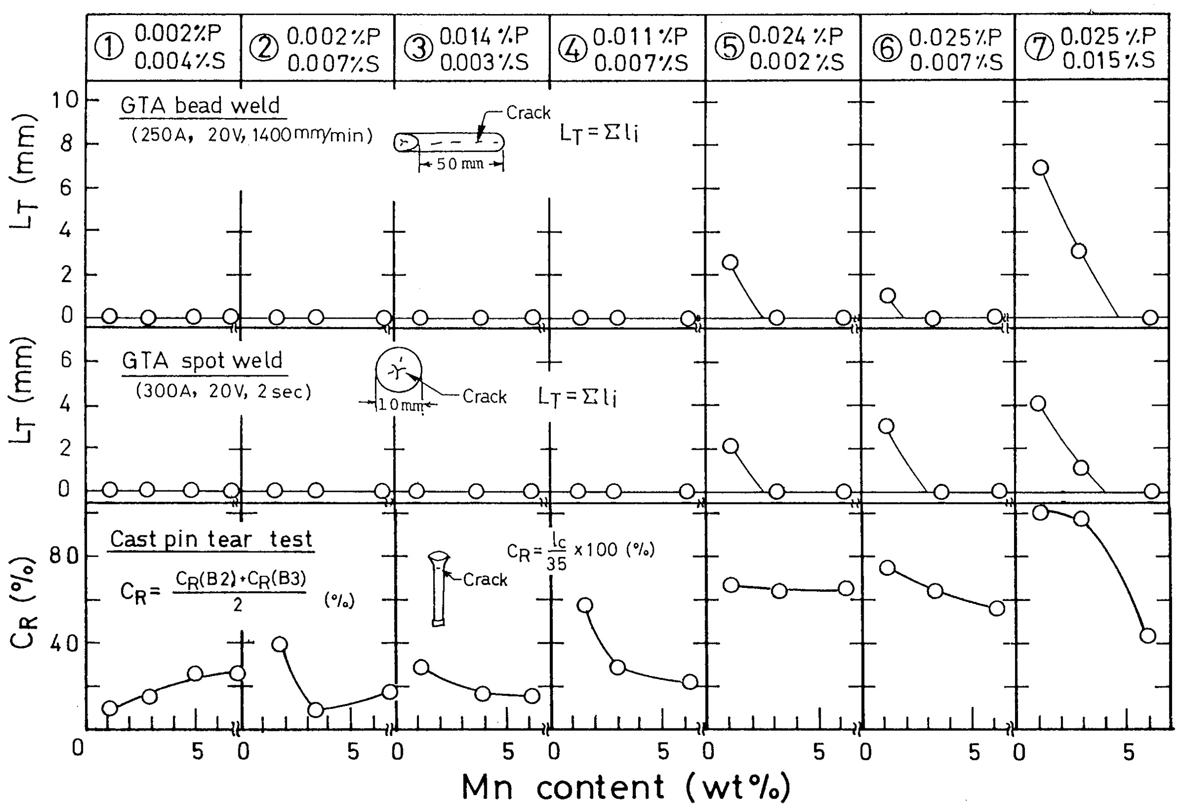

Fig.3 Practical GTA bead and spot weld results and modified CPT test results showing effect of Mn content on cracking susceptibility (L_T, C_R) of SUS310S containing various contents of P and S.

ing was most intensified at 1 to 2%Mn and appeared to be minimal at about 3 or 4 to 6%Mn. **Figure 5** indicates all the results of EB bead-on-plate welding crack test of materials in Table 1. This also demonstrates that cracking occurred at more than 0.018% P+S content and the cracking length was decreased with Mn addition. The optimum Mn content was between about 3 and 6%; however, even this optimum Mn content could not eradicate cracking completely at commercial levels of about 0.025%P (more than 0.026% P+S). From all the above results the optimum content of Mn was determined in **Fig.6** in the relation between P and S content. It could be interpreted on the whole that the addition of Mn was required to reduce cracking particularly at higher S content, the optimum content being between 3 and 6% at commercial levels of about 0.02 to 0.03%P, but about 1%Mn was sufficient for very low P and S content.

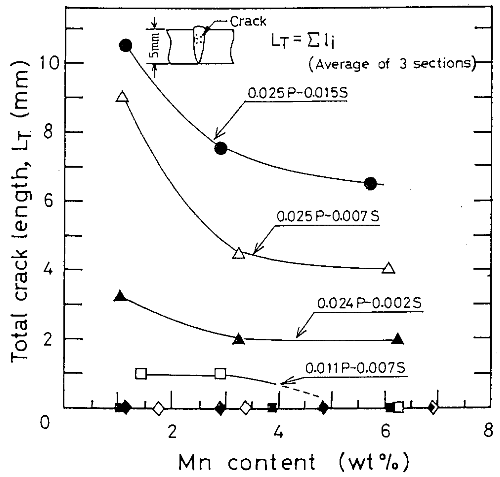

Fig.5 Effect of Mn content on total crack length in EB weld metals of SUS310S containing various contents of P and S.

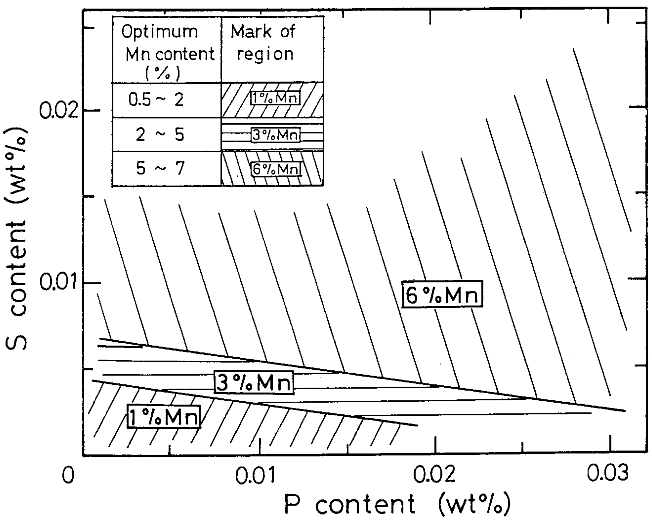

Fig.6 Optimum content of Mn addition determined from several hot cracking test results, expressed in relation of P and S content.

3.1.3 Reason for beneficial effect of Mn

Effect of Mn content on the formation numbers of sulphides and phosphides in weld metals was investigated by employing the SEM and EDX method[13]. The result is provided in **Table 5** with the results of Mn ratio in sulphides and phosphides and nominal T_L and T_S of materials. From these results it is regarded that an increase in Mn content had little or no effect on the formation amounts of sulphides and phosphides but showed a tendency to increase the ratio of Mn to Cr in both sulphides and phosphides. It is therefore induced that the increase in Mn content raises the solidification temperature of sulphides, considering that eutectic temperatures of Mn-MnS and Cr-CrS are about 1580 and 1350°C[16], respectively, and Cr in austenite-(Mn, Cr)S type sulphide[13] is replaced by Mn. On the other hand, the Mn addition is considered to exert action to lower the solidification temperature of phosphides because the eutectic temperature of Mn-Mn_3P, about 960°C[16], is lower than that of austenite-Mn_3P in commercial weld metals, and actually the thermal analysis results of SUS310S containing about 0.5%P and 0.003%S showed that the eutectic temperatures of austenite- $(Cr, Fe, Ni, Mn)_3P$ were approximately 1095 and 1060°C for about 1 and 6%Mn, respectively. Thermal analysis results in Table 5 indicate that T_L and T_S were lower by about 15 to 20°C and 25 to 50°C for about 3 to 6%Mn, respectively, than those for 1%Mn. Such a drop in T_L means a drop in the upper temperature limit of the BTR, which would result in the narrower BTR if the lower temperature limit does not drop.

To provide a better understanding of the effect of Mn on weld metal cracking, on the basis of the above results, the variations in T_L, T_S, solidification temperatures, ${}_sT_S$ and ${}_pT_S$, (shown in a range) of

Table 5 Number of sulphides and phosphides and average ratio of Mn to Cr in inclusions in SUS310S weld metals, in addition to T_L, T_S and T_L-T_S of SUS310S containing various combinations of S and Mn contents.

S level		low				medium		high	
Composition (wt%) / Inclusion	S	0.003	0.003	0.003	0.005	0.015	0.015	0.05	0.05
	P	0.023	0.022	0.022	0.019	0.025	0.025	0.028	0.028
	Mn	1.15	1.9	2.75	4.7	1.1	5.7	1.2	6.5
Number of sulphides		1	4	4	4	120	100	175	180
(Mn ratio)		0.27	0.30	0.30	0.40	0.34	0.53	0.44	0.63
Number of phosphides		39	29	37	20	45	55	65	50
(Mn ratio)		0.19	0.21	0.22	0.27	0.18	0.38	0.19	0.38
Liquidus temp. T_L (°C)		1405	1402	1397	1391	1400	1385	1395	1375
Solidus temp. T_S (°C)		1355	1347	1341	1335	1450	1325	1335	1285
T_L - T_S (°C)		50	55	56	56	50	60	60	90

Investigated area: about 1×10^{-2} mm^2

Mn ratio = (MnK_α counts + CrK_β counts)/ CrK_α counts (EDX result) sulphides and phospides and the BTR according to Mn content are schematically summarized in **Fig.7** (a) and (b) for very low and commercial levels of P and S, together with schematic illustration of solidification morphology and behavior of liquids in SUS310S weld metal containing commercial level of P, S and Mn. T_L and T_S' are the upper and lower temperature limit, respectively, of the BTR. The BTR means the temperature range over which cracking occurs at the solidification grain boundaries in the range of T_L and T_S (see the illustration) and propagates along migrated grain boundaries joining liquid droplets at temperatures below T_S. In the case of very low level of P and S in Fig.7 (a), the BTR decreases, as compared with that for commercial levels of P and S, because of the decrease in the degrees of segregation of P and S and the amount of liquid droplets enriched in P in particular and S; however, since a small number of sulphides were found even at 0.003%S, the solidification temperature range of sulphides,$_sT_S$, is shown as dotted lines, and cracking propagates to a small extent at temperatures below T_S. The reason why an increase in Mn content enlarged the BTR slightly for very low P and S content seems to be associated with the fact that the extent of a drop in T_S is greater than that in T_L. On the other hand, in the case of commercial level of P and S, the BTR enlarges due to increases in P and S, and it is supposed from Fig.7 (b) that the tendency of the lower temperature limit of the BTR appears to be similar to that of solidification temperatures of sulphides instead of nominal T_S. Consequently,it is understood that the Mn addition reduced the BTR, which led to a greater cracking resistance, due to the action that an increase in Mn content caused the T_L to drop and made the solidification temperatures of sulphides rise slightly.

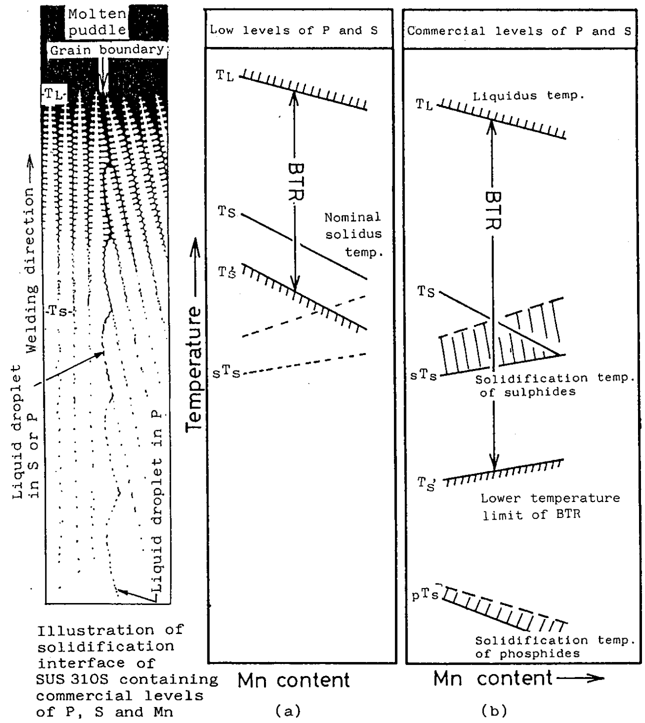

Fig.7 Summary of relations of T_L, T_S, solidification temperatures of sulphides and phosphides and BTR to Mn content for (a)very low P and S and (b)commercial P and S content in addition to schematic illustration of solidification morphology and liquid behavior in commercial SUS310S.

3.2 Effect of N on cracking susceptibility of SUS310S

Figure 8 shows the effect of N on ductility curves for SUS310S weld metals. It indicates that although the N addition did not broaden the BTR at large augmented strains, N exterted a slight influence on the enlargement of the BTR. Therefore it cannot be judged that N has a beneficial effect on cracking resistance. Subsequently, GTA spot welding crack

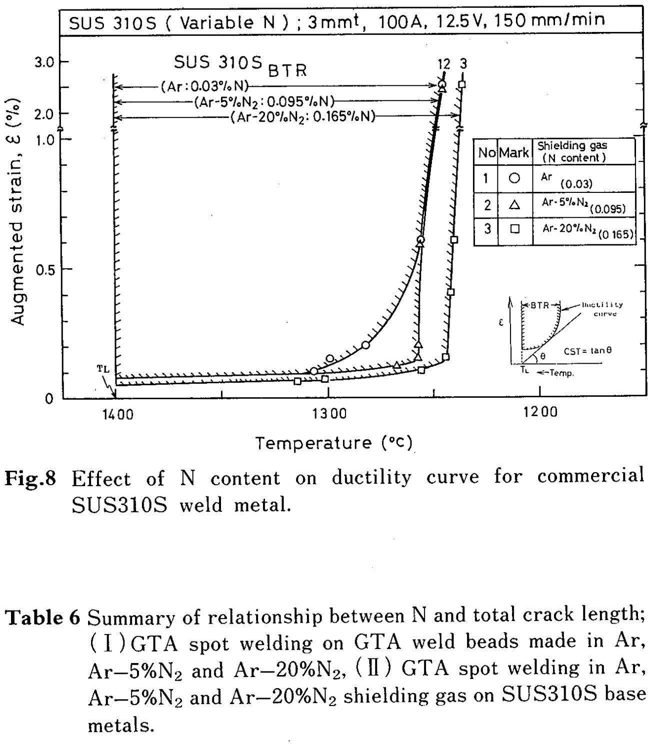

Fig.8 Effect of N content on ductility curve for commercial SUS310S weld metal.

Table 6 Summary of relationship between N and total crack length; (I) GTA spot welding on GTA weld beads made in Ar, Ar–5%N_2 and Ar–20%N_2, (II) GTA spot welding in Ar, Ar–5%N_2 and Ar–20%N_2 shielding gas on SUS310S base metals.

Group	Shielding gas		Total crack length L_T (mm)
	Bead welding,	spot welding	
I	Ar	Ar	8.47
	Ar+5%N_2	Ar	7.98
	Ar+20%N_2	Ar	8.14
	Spot welding		
II	Ar		8.14
	Ar+5%N_2		9.49
	Ar+20%N_2		10.21

test was carried out to confirm the effect of N in practical services. The result is presented in **Table 6.** It can be seen that N did not exert a beneficial effect in minimizing the amount of cracking. From the above results it was found that N would not be so beneficial to the improvement of the cracking susceptibility of SUS310S fully austenitic weld metal as expected beforehand[6),13)].

4. Conclusions

The quantitative effects of Mn and N on the cracking resistance of weld metals of commercial SUS310S fully austenitic stainless steels were investigated by the BTR and the amount of cracking in practical welding. To confirm the effect of Mn the contents of P and S were varied intentionally. The following conclusions can be drawn:

(1) It was found that the optimum Mn content to improve cracking resistance was concerned with the P and S content and needed to be increased from 1 to 6% depending on an increase in P and S content. Especially about 6% Mn was beneficial for more than 0.006%S. In the commercial ranges of 0.02 to 0.03%P and 0.003 to 0.02%S, about 3 to 6%Mn, in particular 6%Mn, was found to be effective. In this case, however, since the degree of the effect of Mn addition decreased with a decrease in S content, the Mn addition could not attain the BTR of less than 150°C nor the degree of improved cracking resistance which could be obtained by reducing the P and S content.

(2) The main reason for the beneficial effect of Mn was attributed to the reduction in the harmful effect of S by forming α-MnS type sulphides of relatively high melting point. If the drop in the liquidus temperature, T_L, means the drop in the coherent temperature[17)], the action that an increase in Mn content caused the T_L to drop may be secondarily contributory to a slight decrease in the BTR and the slight improvement of the cracking resistance.

(3) N was not beneficial enough to prevent or minimize cracking.

Acknowledgement

The authors wish to acknowledge K. Tohmoto, technical assistant of JWRI, for his aid in performing the modified cast-pin-tear test.

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