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Solidification Crack Susceptibility in Weld Metals of Fully Austenitic Stainless Steels (Report V)[†]

— Solidification Crack Susceptibility and Amount of Phosphide and Sulphide in SUS 310S Weld Metals —

Fukuhisa MATSUDA*, Seiji KATAYAMA** and Yoshiaki ARATA*

Abstract

It has been widely known that P and S have a detrimental effect on the cracking susceptibility of austenitic stainless steel weld metals¹⁾. It would be of an economical and technical importance to determine the contents to which P and S can be allowed in weld metals. Previously reported investigation of weld metal crack susceptibility suggested that the P and S content should be each restricted to 0.01% or, if possible, 0.005% in order to minimize or prevent cracking in SUS (AISI) 310S fully austenitic stainless steels²⁾. Moreover, it has been revealed that phosphides and/or sulphides indicative of segregation of P and S resulting from solidification were detrimental to the cracking resistance in weld metals and reheated regions.

In the present work, therefore, metallographic investigation of formation tendency of phosphides and sulphides in the case of low P and S contents was performed by means of energy dispersive x-ray analyses of inclusions and micro-constituents to obtain a better understanding of metallurgical effects of the P and S content on the cracking susceptibility of SUS 310S and, for reference, SUS 304 weld metals. The result indicated that no phosphides were observed in the case of about 0.006%P or less while a negligibly small number of sulphides were observed in the case of 0.003-0.005%S for GTA melt run weld metal of SUS 310S. Consequently, it was significantly confirmed that, in order to achieve the extremely improved cracking resistance of SUS 310S, it is indispensable to reduce P content first of all down to about 0.006% and thereafter it is preferable to reduce S content below about 0.005%.

On the other hand, it was positively understood that one of the main reasons for the excellent crack resistance of SUS 304 is due to the solidification process characteristic of primary solidification of a large amount of delta ferrite, eutectic/peritectic reaction and $\delta \rightarrow \gamma$ transformation behavior.

KEY WORDS: (Austenitic Stainless Steels) (Metallography) (Nonmetals) (Hot Cracking) (Weldability Tests) (Weld Metals)

1. Introduction

Although fully austenitic stainless steels possess excellent corrosion resistance and highly good elevated temperature properties, the fully austenitic weld metals are notorious for the great susceptibility to hot cracking. Therefore, a series of study has been made with the primary objective of developing a fully austenitic stainless steel which would be much more resistant to weld cracking. SUS 310S (corresponding to AISI 310S) has been consistently used as a typical fully austenitic alloy occasionally by contrast with SUS 304 (AISI 304) containing some delta (δ) ferrite in austenite (γ) which is highly resistant to cracking.

According to the fundamental investigation³⁾ of the microstructures and microsegregation in the weld metals

quenched rapidly during weld-solidification, it is revealed that SUS 310S solidifies as austenite phase in the whole process of solidification in the weld metal, with the result that impurities such as phosphorus (P), sulphur (S), etc., segregate to a great extent at the final intergranular sites. On the basis of the results⁴⁾ obtained by using the Trans-Varestraint test and fractographic and metallographic techniques, commercially available SUS 310S with about 0.021%P and 0.007%S is characteristic of the wide brittleness temperature range (BTR) of about 1400-1240°C, in which a feature of solidification crack surface morphology varies gradually from a dendritic mode to a smooth appearance with a reduction in temperature mainly because solidification cracking initiates primarily along columnar grain boundaries over the range of about

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1400-1310°C according to augmented-strain rate and down to about 1240°C propagates along migrated grain boundaries joining low-melting-point liquid lakes enclosed in the solid. The greater part of such low-melting-point lakes must successively form sulphides at about 1320-1280°C and/or phosphides at about 1100-1060°C⁵⁾. Moreover, based on the experimental result²⁾ that P and S have detrimental effect on the susceptibility to solidification cracking, compositional recommendations are made for further improvement on SUS 310S as follows: P and S should each be reduced down to 0.01% or less, or more favorably below 0.005%, if possible, and in this case a decrease in Si and C seems to be slightly beneficial.

Therefore, in this paper a microstructural investigation of the formation tendency of phosphides and/or sulphides in SUS 310S weld metals containing about 0.001-0.023%P and 0.003-0.017%S was performed to provide a better understanding of allowable contents of P and S in terms of solidification crack prevention in practical production welding. The background of this investigation is that an appreciable number of phosphides and sulphides can imply the degree of microsegregation of P and S as well as existence of low-melting-point liquid pockets. Furthermore, the major cause conducive to weld cracking

in the solidification process of austenite alone in SUS 310S is attributed to the higher degree of the segregation of impurities and the existence of liquid pockets during weld-solidification, which reasonably result in depressing significantly both the solidus temperature and the cracking propagation-arrest temperature. In addition, inclusions such as phosphides and sulphides have been considered to be the major cause in liquation cracking in the heat-affected zone (HAZ) adjacent to the fusion boundary and in the underlying weld metal reheated by subsequent pass.^{1), 6) - 9)} From the above points of view the quantitative measurement of such inclusions would be expected to help to solve the weld cracking problem in practical production.

2. Materials and Experimental Procedure

The chemical compositions of materials used are given in Table 1. Identification of phosphides and sulphides in weld metal was made on commercial SUS 310S-(1), by using conventional carbon-extraction replicas with the help of electron diffraction (ED) method of transmission electron microscopy (TEM) and energy dispersive x-ray spectrometer analysis (EDX) method of scanning electron

Table 1 Chemical compositions of materials investigated.

Group	Materials (SUS, AISI)	Composition (wt%)								
		C	Si	Mn	P	S	Cr	Ni	N	O
I	310S-(1)	0.078	0.93	1.56	0.021	0.007	25.06	20.30	0.029	0.015
	310S-(2)	0.070	0.73	1.05	0.022	0.017	24.45	19.90	0.033	0.027
	310S-(3)	0.063	0.69	1.15	0.023	0.003	24.60	20.20	0.052	0.043
	310S-(4)	0.053	0.54	1.33	0.013	0.012	25.05	19.94	0.053	0.030
	310S-(5)	0.067	0.51	1.47	0.007	0.007	24.92	19.97	0.016	0.017
	310S-(6)	0.068	0.22	1.46	0.005	0.009	24.99	19.85	0.016	0.025
	310S-(7)	0.071	0.11	1.44	0.006	0.007	24.99	20.08	0.017	0.025
	310S-(8)	0.052	0.13	1.36	0.003	0.009	24.68	20.28	0.002	0.026
	310S-(9)	0.014	<0.01	1.41	0.002	0.003	23.88	21.13	0.048	0.024
	310S-(10)	0.060	0.55	0.97	0.001	0.003	24.62	19.52	0.020	0.005
	310S-(11)	<0.05	<0.01	<0.01	0.002	0.005	24.45	20.31	0.008	0.034
II	304-(1)	0.052	0.75	0.97	0.026	0.005	18.26	8.97	0.019	0.005
	304-(2)	0.072	0.52	0.91	0.030	0.005	18.12	8.74	0.023	0.008
	304-(3)	0.070	0.70	1.18	0.027	0.010	18.26	8.44	0.025	0.014
	304-(4)	0.05	0.58	0.94	0.057	0.006	18.50	9.10	0.026	—
	304-(5)	0.06	0.61	0.99	0.121	0.005	18.60	9.10	0.021	—
	304-(6)	0.06	0.60	1.00	0.249	0.005	18.55	9.05	0.026	—
	304-(7)	0.06	0.56	0.94	0.025	0.220	18.50	9.10	0.030	—
III	310S-(12)	0.066	0.56	1.41	0.032	0.013	24.70	19.86	0.024	0.034
	310S-(13)	0.082	0.94	1.58	0.022	0.007	24.45	19.90	0.028	0.015
	310S-(14)	0.066	0.66	1.48	0.022	0.007	24.59	20.03	0.024	0.033
	310S-(15)	0.070	0.53	0.83	0.022	0.004	25.35	19.80	0.041	0.059
	310S-(16)	0.065	0.74	1.55	0.012	0.008	24.85	20.05	0.031	0.010
	310S-(17)	0.070	1.03	1.44	0.008	0.008	24.84	20.01	0.020	0.005
	310S-(18)	0.068	0.31	1.48	0.006	0.007	24.87	19.90	0.07	0.020
	310S-(19)	0.070	0.67	1.62	0.002	0.010	25.30	19.60	0.003	0.011
	310S-(20)	0.016	<0.01	1.41	0.002	0.003	24.67	20.78	0.038	0.018
IV	310S-(21)	0.07	0.70	1.07	0.023	0.012	24.65	20.10	—	—
	310S-(22)	0.07	0.97	1.44	0.023	0.005	24.81	20.00	—	—

microscopy (SEM). Measurements of phosphide and sulphide contents in weld metals were carried out with SEM observation and EDX method on 11 different heats of SUS 310S-(1) to SUS 310S-(11) fully austenitic stainless steels in Group I and for reference, 5 different heats of SUS 304-(1) to SUS 304-(5) duplex stainless steels in Group II, which contained a variety of P and S levels. It should be noted that the P and S levels of SUS 310S were in the low range of 0.001-0.023% and 0.003-0.017%, respectively. Weld metals were produced on 3 mm thick square (100 x 100 mm) or round (100 mm ϕ) sheets by quenching during or after GTA bead-on-plate welding with no filler metals under the conditions of welding current 100 A (DCSP), welding voltage 12.5 V and welding speed 150 mm/min. The Trans-Varestraint test, modified Houldcroft-type hot cracking test, and GTA and resistance spot weldings were performed on the materials in Group I, II and III to assess the effects of P and S on cracking susceptibility. The details of each experimental procedure and welding conditions are the same as those of the previous paper²⁾ reported. Moreover, electron beam welding (EBW) was conducted on 3 different heats of SUS 310S-(10) and SUS 310S-(21) and (22) 12 mm thick plates (100 x 50 mm) in Group IV and SUS 304-(4) to (7) 20 mm thick disk plates (100 mm) in Group II under 2 different conditions of 150 kV, 40 or 30 mA and 2000 or 1000 mm/min.

3. Results and Discussion

3.1. Identification of phosphide and sulphide in SUS 310S weld metal

Figure 1 shows the SEM microstructure obtained from the polished and etched sample of commercial SUS 310S-(1) (3 x 100 x 100 mm) weld metal containing about 0.021%P and 0.007%S, welded with no filler metals with GTA parameters of 100 A, 12.5 V and 150 mm/min in Ar

atmosphere. White microconstituents formed at cellular dendritic and grain boundaries in this figure were analyzed by the EDX of SEM. From the results, examples of which are shown in Fig. 2, it was noticed that these phases were enriched in P and/or S with respect to the matrix of austenite. The phases rich in P or S were, consequently, judged to be phosphides or sulphides, as revealed more distinctly in the following. Phosphides and sulphides were both in globular, granular or oval shape and in general about 0.4-0.8 μ and 0.3-0.6 μ in size, respectively. Figure 3 shows the SEM microstructure of carbon-extraction replica film from above mentioned SUS 310S-(1) weld metal. White particles observed were also analyzed by the EDX. Examples of the analytical results are demonstrated in Fig. 4, where the detection of Cu count peaks didn't come from small particles but was due to Cu mesh and/or Cu meshholder. From these results, it is readily observed that phosphides and sulphides were undoubtedly extracted from cellular dendritic and columnar grain boundaries. They were subsequently observed through TEM and

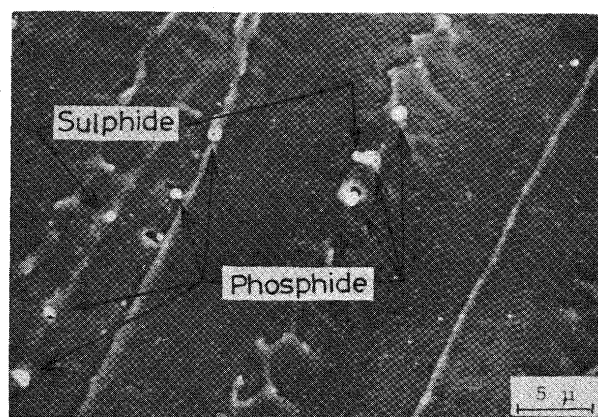


Fig. 1 SEM microstructure of SUS 310S-(1) weld metal containing 0.021%P and 0.007%S, showing formation of phosphides and sulphides at cellular dendritic and columnar grain boundaries.

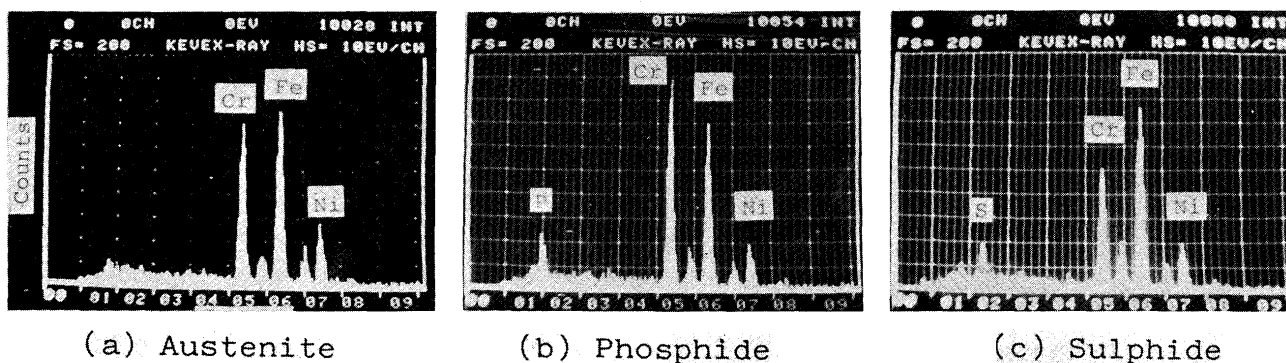


Fig. 2 EDX results for austenite (a) and microconstituents (b) and (c) in SUS 310S-(1) weld metal, showing an enrichment of P or S in constituents.

identified with ED method. The results as regards phosphides and sulphides are shown in Figs. 5 and 6: (a), (b) and (c) exhibit TEM micrograph, ED pattern taken from an inclusion in (a) and the key-diagram of (b), respectively. Based on the results of Figs. 4 and 5, phosphides were identified as M_3P type rich mainly in Cr and P, containing an appreciable amount of Fe, Ni, etc. (therefore, M represents Cr, Fe, Ni, etc.). Similarly from Figs. 4 and 6 sulphides were identified as α -MnS type rich predominantly in S, Mn and Cr. These results confirm that the structure and the chemical composition of phosphides and sulphides in commercial SUS 310S weld metal are much the same as those of phosphides and sulphides in SUS 310S type weld metals containing about 0.1-0.2%P or 0.2%S as stated in the previous paper⁵).

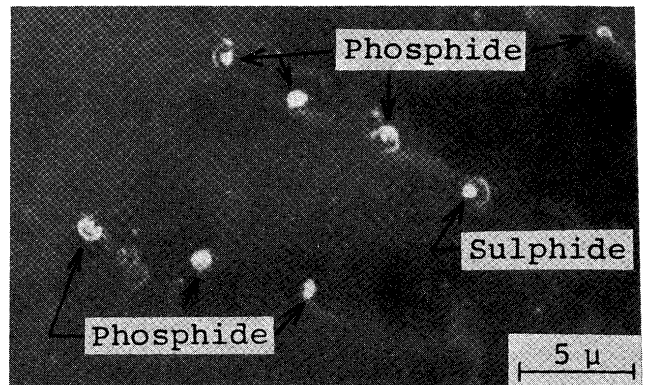
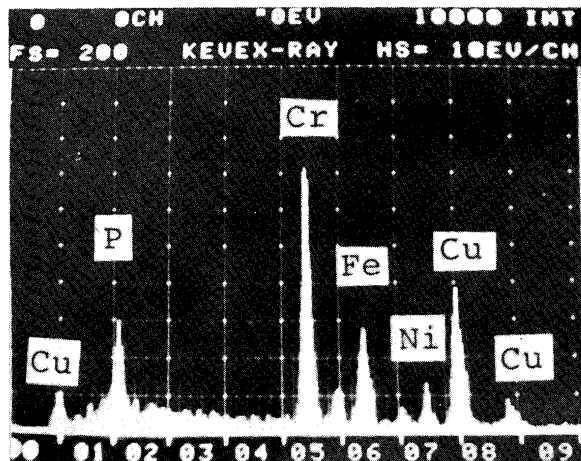
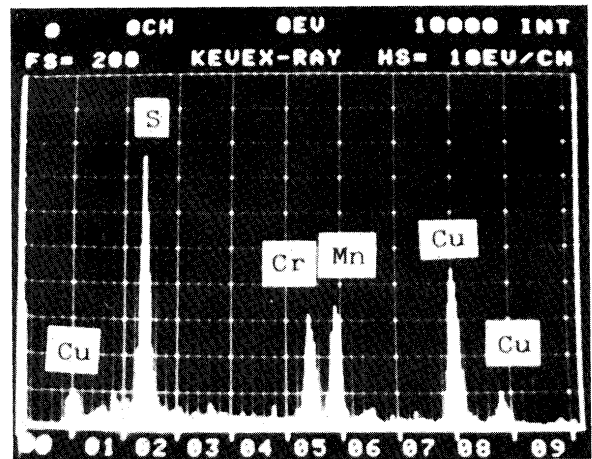


Fig. 3 SEM micrograph of carbon-extraction replica film from SUS 310S(1) weld metal, showing successful extraction of small particles such as phosphides and sulphides.

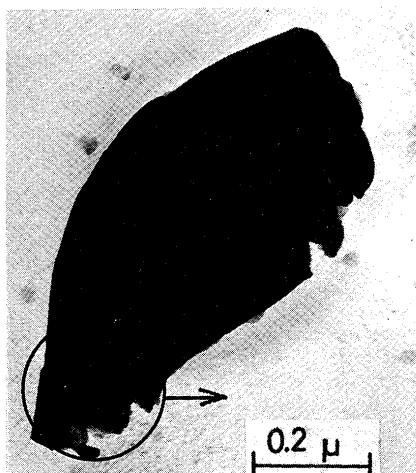


(a) Phosphide

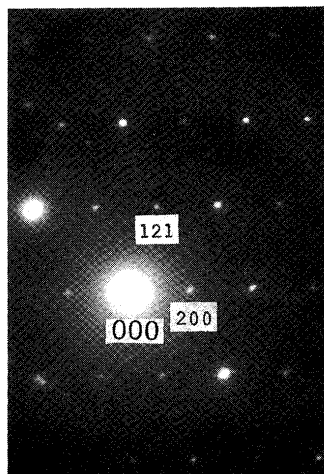


(b) Sulphide

Fig. 4 EDX results of small particles on replica film, showing an enrichment of Cr, Fe, Ni and P (a) or Mn, Cr and S (b) in particles. Peaks of Cu counts are due to Cu mesh and/or Cu holder irrelevant to particles.



(a) Phosphide



(b) Electron diffraction (c) Key-diagram pattern

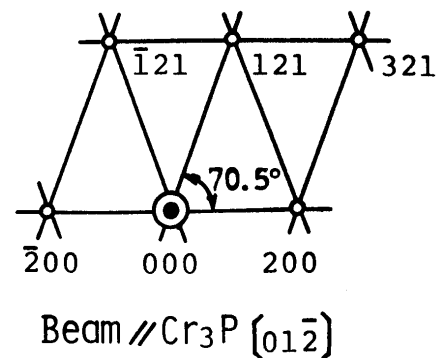


Fig. 5 TEM microstructure (a), electron diffraction pattern (b) and key-diagram of (b) (c) of phosphide on replica film from SUS 310S(1) weld metal, indicating formation of M_3P type phosphide.

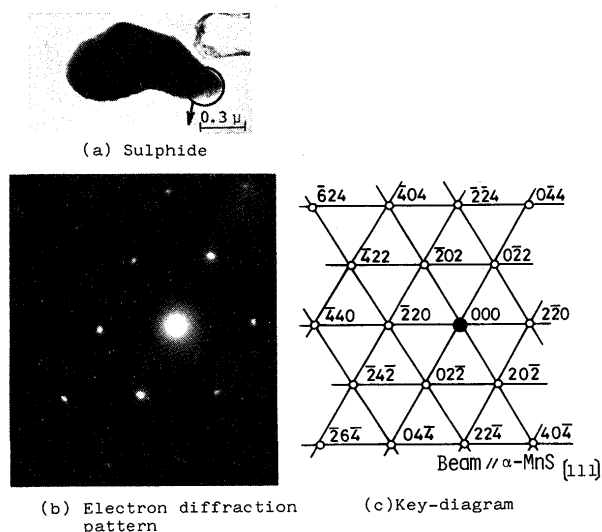


Fig. 6 TEM microstructure (a), electron diffraction pattern (b) of sulphide and its key-diagram (c), indicating formation α -Mns type sulphide.

Thus, it is reasonable to expect that the solidification temperatures or melting points of phosphides and sulphides in commercial SUS 310S must be roughly the same as those of SUS 310S with a large amount of P and S, respectively. Moreover, from the EDX analytical result it was confirmed that although SUS 310S contained approx. 55%Fe and 20%Ni, FeS and Ni_xS_y (such as Ni_3S_2) type sulphides were not detected in particular, chiefly because S has a much more potent tendency to combining with Mn and Cr as well known.^{1), 7), 8)} It was otherwise found that CrS type sulphides only depleted in Mn, Fe and Ni actually formed in the special case of less than 0.01%Mn in SUS 310S-(11). This example of EDX results is given in Fig. 7. The EDX results are consistent with the result¹⁰⁾ that Mn, Cr, Fe and Ni are rated in

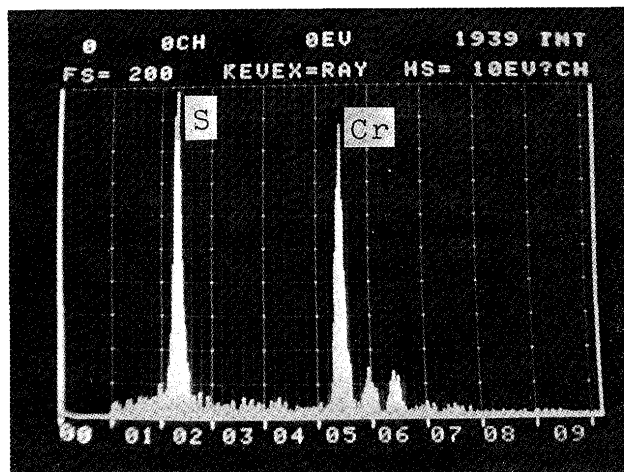


Fig. 7 EDX result of sulphide in SUS 310S-(11) weld metal containing less than 0.01%Mn.

decreasing order of the tendency to combining with S. Therefore, it may be reasonable to exclude every possibility of the formation of FeS and Ni_xS_y and their eutectics of low melting points in austenitic stainless steels since a considerable amount of Cr and a small amount of Mn are commonly included.

3.2. Effect of phosphorus and sulphur on phosphide and sulphide amount in SUS 310S weld metals

The paper in which the formation numbers of phosphides or sulphides were quantitatively investigated in weld metals containing a small amount of P and S has hardly been reported up to the present. Therefore, in this section the numbers of phosphides and sulphides were determined in SUS 310S melt run weld metals containing about 0.001 to 0.023%P and 0.003 to 0.017%S, by employing a combination of SEM observation ($\times 10,000$) and EDX analyses of inclusions observed in a view area of $12 \times 8 \mu$, as has been shown in Figs. 1 and 2, respectively. Table 2 summarizes the counts of inclusions rich in P and/or S in sizes from 0.2 to more than 1.0μ according to given temperature ranges in commercial SUS 310S-(1) weld metal quenched during GTA welding. From this result it is deduced that variations in the counts of phosphides and sulphides in each size range according to a drop in temperature are small enough to be tolerated except for more or less broad scattering in the sizes of phosphides in the ranges quenched from about 1350-1300°C. This exception is probably because phosphides at about 1350-1300°C formed by quenching from the state of liquid film at boundaries, on the basis of the melting points of phosphides and sulphides being about 1100-1060°C and 1320-1280°C, respectively⁵⁾. Nevertheless, there seems to be little significant difference in the total number of phosphides and sulphides between respective temperature ranges.

Table 3 summarizes the counts of phosphides and sulphides in five divisional size ranges for respective almost equal levels of P and S contents in SUS 310S weld metals. Figure 8 also shows the relationship between P or S content and the number of phosphides or sulphides in SUS 310S type weld metals both quenched from 1250-1200°C and partly cooled normally to room temperature, in addition to the result of SUS 304 type weld metals for comparison. In the case of SUS 310S weld metals, it is clear that the numbers of phosphides and sulphides, particularly the larger ones in size, are both increasing with an increase in P and S content. Moreover, comparison of the formation amount between phosphides and sulphides at equal levels of P and S content in SUS 310S easily reveals that the amount of sulphide is larger than that of phosphide. Furthermore, concerning the

formation limit of phosphides and sulphides, no phosphides were detected in weld metals containing about 0.006% and less by the SEM observation (x2,000-10,000), while a small number of sulphides were observed even at approximately 0.003%S. However, in commercial SUS 310S weld metal containing 0.021%P and 0.007%S, it was found that the amount of phosphides observed was

greater than that of sulphides, because S content was reduced to a lesser extent than P content during refining.

On the other hand, in the case of SUS 304 type weld metals, no phosphides were detected at P content of about 0.06% and less whereas a small number of sulphides were observed even at about 0.005%S. This means that S has a predominantly greater tendency towards micro-

Table 2 Summary of counts of inclusions enriched in P or S (per area of 0.096 mm²) according to sizes and given temperature ranges.

Temperature range at quenching (°C)	Elements rich in inclusions	Size (longest length; l) (μ)					Counts of inclusions
		$0.2 \leq l < 0.4$	$0.4 \leq l < 0.6$	$0.6 \leq l < 0.8$	$0.8 \leq l < 1.0$	$l \geq 1.0$	
1350 - 1300	Cr, P	7	12	8	2	9	38
	Mn, S	2	4	1	0	1	8
	P, S	0	5	1	0	0	6
1250 - 1200	Cr, P	1	8	17	4	2	32
	Mn, S	5	1	2	0	0	8
	P, S	0	3	1	1	0	5
900 - 800	Cr, P	0	10	14	6	3	33
	Mn, S	6	3	1	0	0	10
	P, S	0	2	1	1	0	4
room temperature	Cr, P	1	13	16	5	5	40
	Mn, S	6	3	0	0	0	9
	P, S	0	0	2	0	0	2

Table 3 Summary of counts of inclusions enriched in P and/or S in SUS 310S weld metals, showing difference in formation tendency between phosphides and sulphides at respective similar levels of P and S contents.

size (μ) P content (%)	Number of phosphides (count/0.0096mm ²)					size (μ) S content (%)	Number of sulphides (count/0.0096mm ²)				
	$0.2 \leq l$	$0.4 \leq l$	$0.6 \leq l$	$0.8 \leq l$	$l \geq 1.0$		$0.2 \leq l$	$0.4 \leq l$	$0.6 \leq l$	$0.8 \leq l$	$l \geq 1.0$
	< 0.4	< 0.6	< 0.8	< 1.0			< 0.4	< 0.6	< 0.8	< 1.0	
0.003	0	0	0	0	0	0.003	1	1	0	0	0
0.007	0	1	1	0	0	0.007	6	3	2	0	0
0.013	0	6	4	1	0	0.012	8	20	15	5	0
0.021	1	13	18	5	5	0.017	32	55	36	16	26

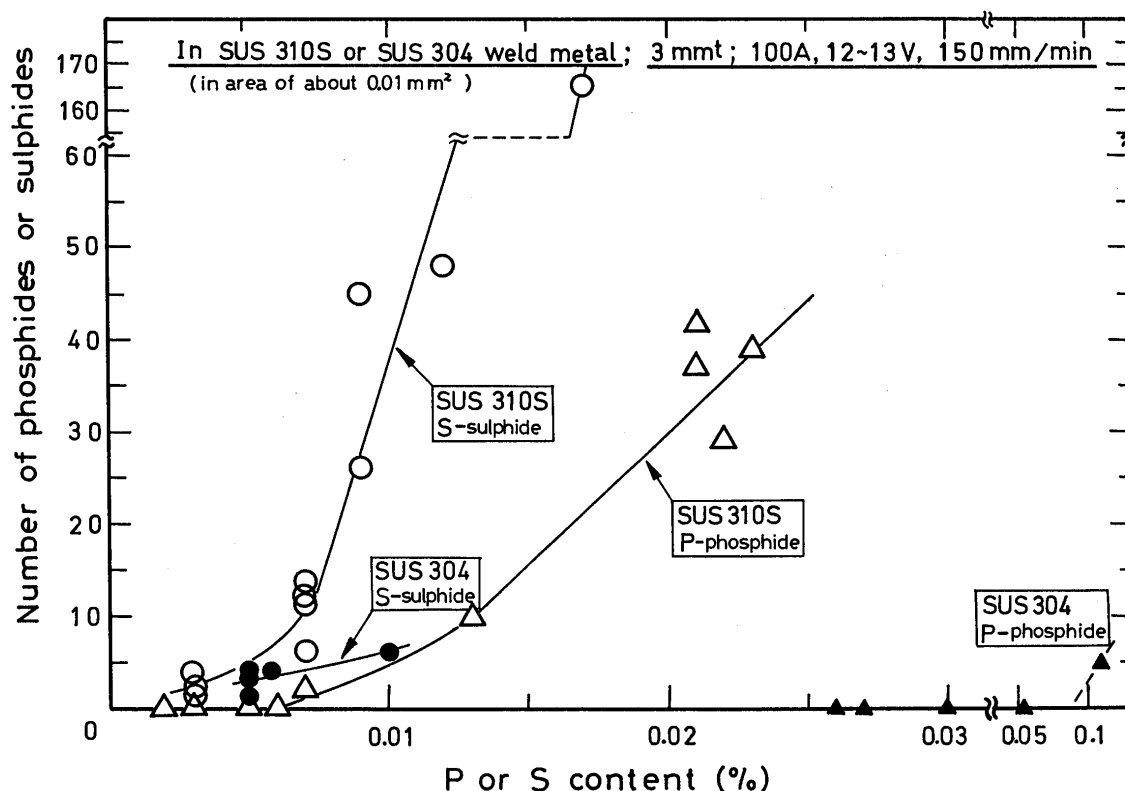


Fig. 8 Relation of P or S content to number of phosphides or sulphides formed in area of about 0.01 mm² in SUS 310S and SUS 304 weld metals.

segregation at boundaries than P in SUS 304 weld metals. In other words, as far as commercial levels of P contents in SUS 304 weld metals are concerned, the microsegregation of P can be reduced due to the primary solidification of delta ferrite to so markedly lesser degrees that the influence of the P contents on the cracking susceptibility can be regarded as a much more negligible effect.

From the above-mentioned results it is generally concluded that more sulphides are observed than phosphides in both SUS 310S and SUS 304 weld metals containing the same levels of P and S contents. Furthermore, it should be particularly noted that more phosphides form than sulphides in commercial SUS 310S weld metal with about 0.021%P and 0.007%S.

3.3. Effect of decrease in P and S on solidification crack susceptibility

Solidification ductility curve, which is considered to be the most reasonable principle in assessing the solidification crack susceptibility at present,^{4)-6), 11), 12)} was obtained for every material shown in Table 1 by the Trans-Varestraint test. Figure 9 is an example of the ductility curves for 5 different heats of SUS 310S containing 0.001-0.032%P and, for reference, commercial SUS 304 with 0.027%P and 0.010%S. It shows a gradual in-

crease in the critical strain rate for a temperature drop (CST) incidental to a gradual reduction in the solidification brittleness temperature range (BTR) with a decrease in P content for SUS 310S. Further, SUS 310S containing approx. 0.001%P and 0.003%S exhibits the extremely improved property of the ductility curve—the narrowest BTR and the greatest CST value of SUS 310S type steels in the figure; however, even its ductility curve property is readily judged to be inferior to that of SUS 304. This difference is attributed to a difference in the solidification processes between SUS 310S and SUS 304. That is to say, the excellent property of ductility curve for SUS 304, meaning actually high cracking resistance, is interpreted in terms of the primarily important effect of the eutectic/peritectic reaction and $\delta \rightarrow \gamma$ transformation behavior on the arrest of cracking propagation in addition to the beneficial effect of a large amount of primary ferrite on the decrease in the microsegregation of impurities, as proposed in the previous paper¹³⁾. Since the BTR corresponded inversely-proportionally to the CST value leading reasonably to the assessment of the solidification crack susceptibility, the BTR would be utilized as an index of the evaluation of cracking susceptibility in the following investigation owing to a smaller number of samples and easier measurement. Figure 10 (a) and (b)

shows the effect of a decrease in P and S content, respectively, on the BTR at $\epsilon = 0.3$, 2.5 and 3.75% of SUS 310S weld metals. According to this figure, BTR of about 125 ($\epsilon = 0.3\%$) – 175°C ($\epsilon = 3.75\%$) for commercial SUS 310S decreases to about 95-120°C and about 120-160°C with a decrease in P and S content, respectively. As a result it is concluded to be indispensable to reduce P content first of all in order to decrease BTR, or to improve cracking resistance, of commercial SUS 310S available in Japan at present. Moreover, it is adequately considered that the influence of S content of 0.007-0.01% or P content of 0.021-0.023% cannot be neglected in the respective case of the materials with P and S content decreased separately. Hence, the distribution of the BTR for SUS 310S with different P and S contents is shown in Fig. 11. As reported in the previous paper²⁾, it is appreciated that the BTR is strongly dependent on the P content at commercial levels of P and S as well as that both P and S equivalently exhibit a harmful influence on an increase in the BTR in the decreased range of both contents.

Subsequently, a more rigorous examination of the effect of chemical compositions including other elements on BTR was undertaken from a multiple linear-regression

analysis of the results of 19 kinds of SUS 310S specimens. The equation linking BTR (°C) at $\epsilon = 2.5\%$ in the Trans-Varestraint test to composition in wt% is expressed below.

$$\begin{aligned} \text{BTR (°C) (at } \epsilon = 2.5\%) = & 3313\text{P} + 1568\text{S} + 184\text{C} \\ & + 2.4\text{Si} - 11.3\text{Mn} - 461\text{N} \\ & + 98.6 \quad \dots\dots (1) \end{aligned}$$

The ranges of chemical compositions obtained for the above equation, with the standard deviation of 6.0°C and multiple correlation of 0.98, are approximately 0.01-0.08% for C, <1% for Si, 0.8-1.6% for Mn, <0.03% for P, <0.02% for S, 24.5-25.5% for Cr, 19.5-21% for Ni, <0.055% for N and <0.06% for O. This formula (1) immediately confirms that increases in P, in particular, and S contents exert a much more detrimental effect on cracking susceptibility, which is in good accord with the results reported by other authors up to the present.¹⁴⁾⁻¹⁸⁾ It also indicates that C and Si have a positive but much smaller effect on the BTR and Mn and N appear to have a little favourable influence. (Therefore, the effect of an increase in Mn or N was separately determined, so that particularly about 3-6% Mn had a beneficial effect only in the case of S content of more than 0.01% but N has a

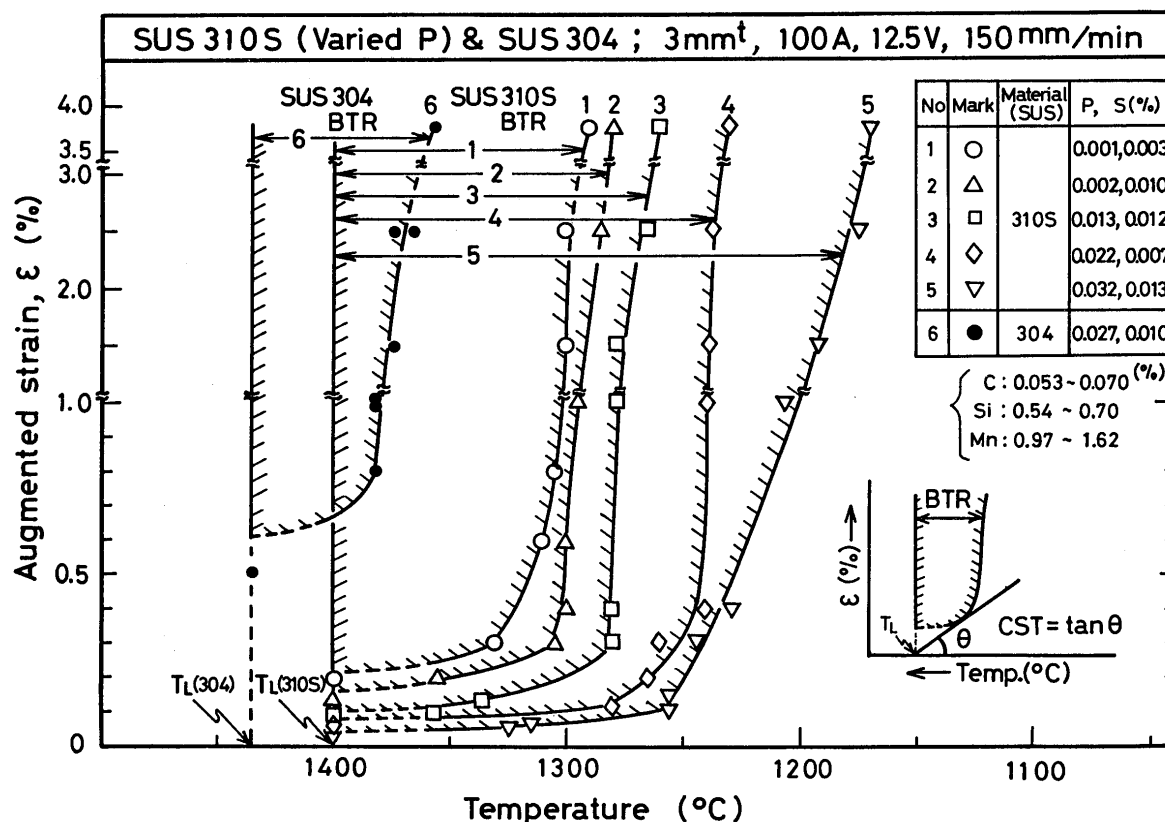


Fig. 9 Effect of decrease in P content on ductility curves for SUS 310S weld metals in contrast to ductility curve for commercial SUS 304 weld metal.

negligible influence in the range of N content of less than 0.2%, as may be discussed in the following paper.) However, based on an ordinary variation in chemical compositions of heats to heats, it is evident that the BTR or the cracking susceptibility is predominantly influenced by P and S contents.

On the other hand, from the viewpoint of practical

production, other empirical experiments and conventional hot cracking test were carried out. Figure 12 shows the relationship between BTR at $\epsilon = 2.5\%$ and the cracking susceptibility of SUS 310S weld metals obtained by modified Houldcroft-type test and in both GTA and resistance spot welds. It is apparent that the crack susceptibility decreases step by step with decreasing the BTR

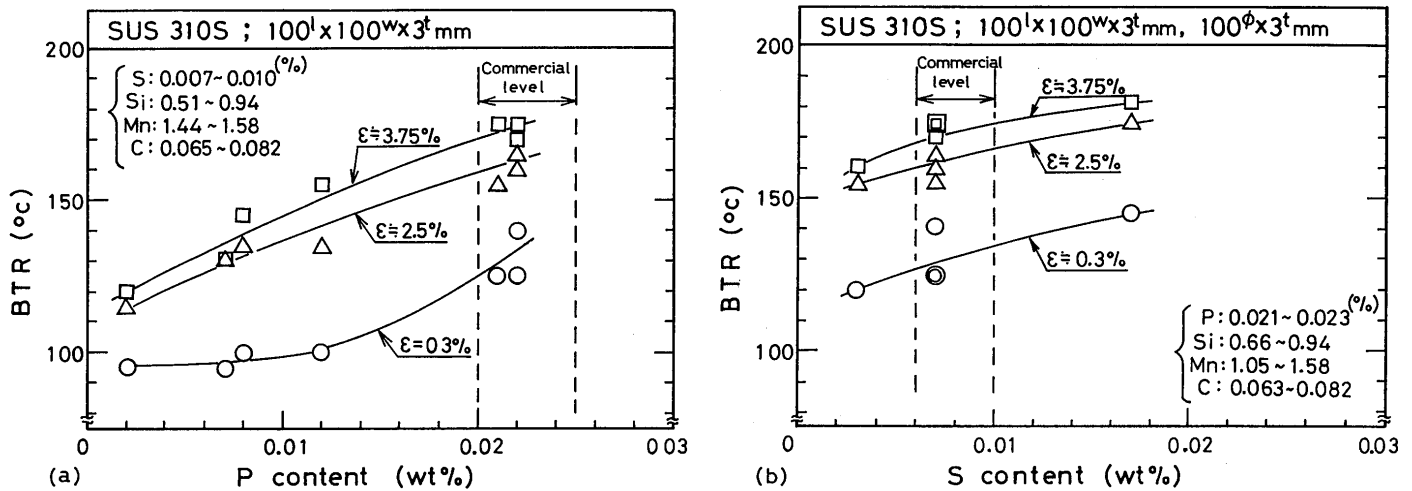


Fig. 10 Effect of decrease in P or S content on BTR at $\epsilon = 0.3, 2.5$ and 3.75% for SUS 310S weld metals.

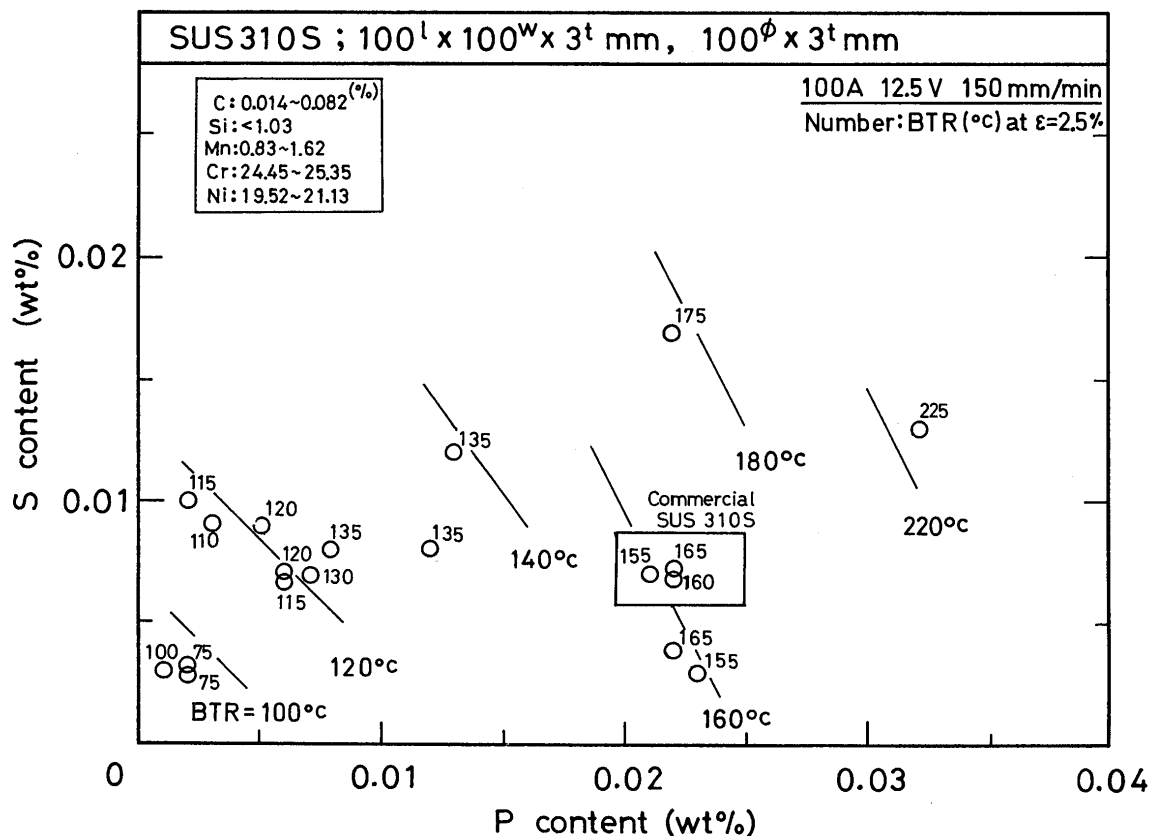


Fig. 11 Effect of P and S content on BTR at $\epsilon = 2.5\%$ for SUS 310S weld metals.

in any case. It should be noted that in GTA spot welds no cracks occurred in the case of BTR of about 130°C and less, and that from the results of both modified Houldcroft-type test and resistance spot welds the cracking resistance was more significantly improved for BTR of less than 110°C. It is suggested from the representation of Fig. 11 that the indispensable condition of such BTR should be attained in the case of less than 0.007%P and less than 0.01%S or, for further improvement, in the case of (P + S) content of less than 0.01%.

For the purpose of confirming whether modified SUS 310S with low P and S content avoids or undergoes solidification cracking in electron beam welds, electron beam welding (EBW) was conducted on SUS 310S plates of 12 mm in thickness with three levels of P + S content. It was generally recognized that horizontal crackings would tend to occur as welding speed got higher and penetration depth got deeper. Figure 13 shows the EBW results of cracking susceptibility under two welding conditions. No cracks were observed in the modified SUS 310S weld metals with 0.001%P and 0.003%S, although each weld metal of commercial SUS 310S with 0.023%P-0.012%S and 0.023%P-0.005%S showed cracks in its degree. Consequently, it was found that extremely low P and S content is highly effective in preventing cracking in SUS 310S weld metals of EBW.

On the other hand, EBW was carried out on SUS 304-(4) to (7) for 0.025-0.25%P and/or 0.005-0.22%S, with the result that the weld metals were free from cracks independently of the P and S contents.

3.4. Correlation of formation behavior of phosphides and sulphides with cracking susceptibility

The distribution of the BTR was discussed in the relation between phosphide and sulphide content which were counted by means of SEM observation and EDX method as described in Table 2 and 3 in 3.2. The result is shown in Fig. 14, representing the BTR(°C) of SUS 310S and, for reference, SUS 304 in terms of the total counts (per an area of about 0.01 mm²) of phosphides and sulphides. It explicitly demonstrates that phosphide amount essentially exerts a much greater influence on the enlargement in the BTR of SUS 310S. This is probably because the solidification temperatures of the liquid films and pockets enriched in P are lower by as much as about 250°C than the nominal solidus temperature of austenite in SUS 310S in contrast to the case that those enriched in S are lower by about 10-50°C. It is positively established that, in order to improve the cracking resistance of commercial SUS 310S, it is significant to reduce P content first of all down to about 0.006% corresponding to no observation of phosphides and subsequently it is prefer-

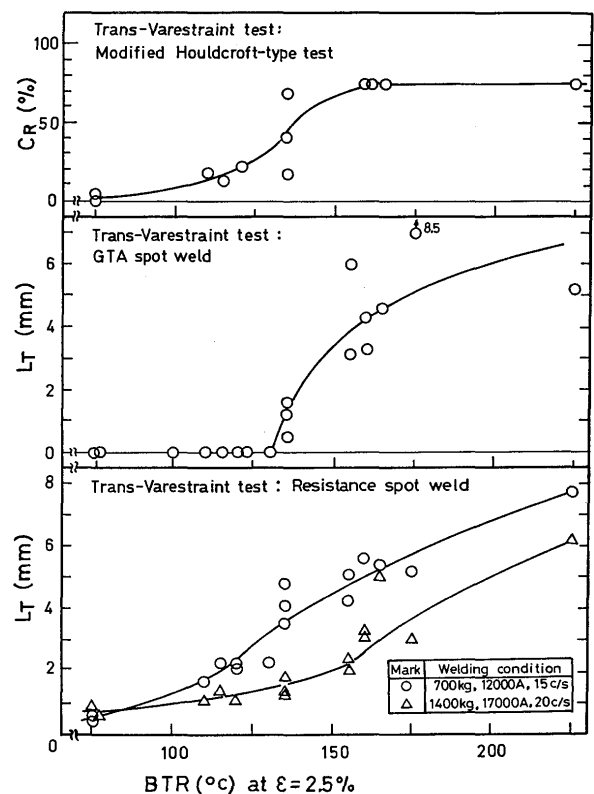


Fig. 12 Relation between BTR at $\epsilon = 2.5\%$ in Trans-Varestraint test and cracking susceptibilities of SUS 310S weld metals in modified Houldcroft-type test and practical spot welds.

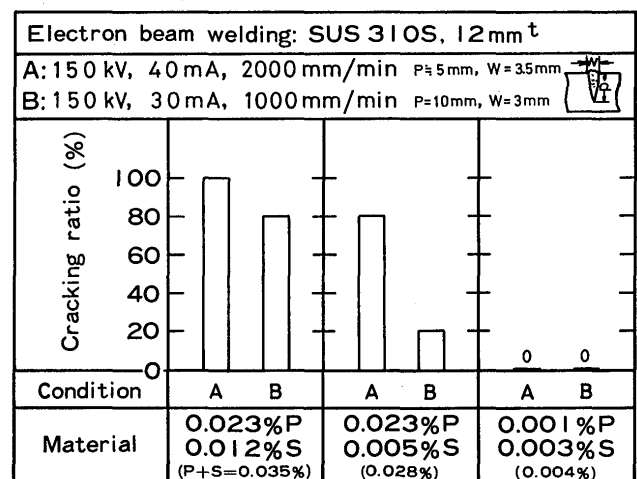


Fig. 13 Effect of decrease in P and/or S content on horizontal crack susceptibility of electron beam weld metal of SUS 310S.

able to decrease S content to less than 0.005% resulting in a negligible number of sulphides only in the case of P content of 0.006% and below. On the other hand, it is to be noted that the BTR of SUS 304 is still narrower than that of any type of SUS 310S in spite of the formation of a small quantity of phosphides and/or

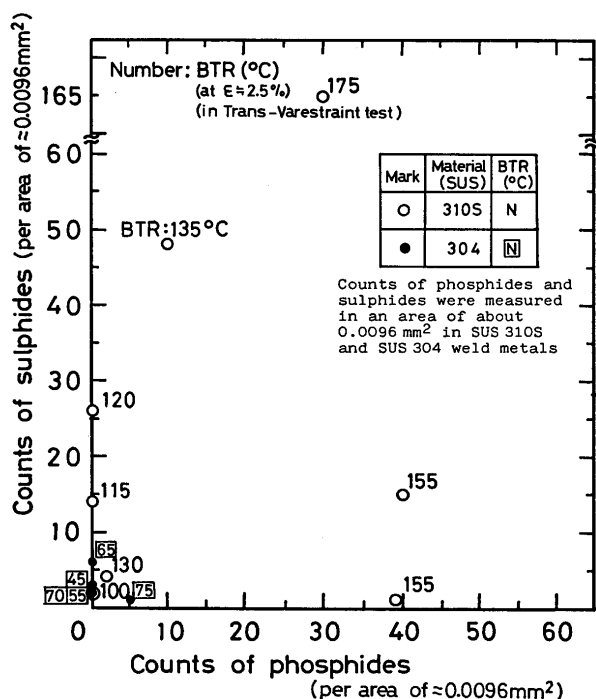


Fig. 14 Relationship between BTR at $\epsilon = 2.5\%$ and counts of phosphides and/or sulphides formed in area of about 0.01 mm^2 for SUS 310S and SUS 304 weld metals.

sulphides in weld metals. This sufficiently means that the reason is attributed to the favorable effect of the solidification process of SUS 304, as has been discussed in the previous paper^{1,3)} in detail. That is to say, it is actually understood that the effect of a large amount of primary delta ferrite alone on the decrease in the segregation of P, S, etc., is not necessarily the most advantageous to the narrow BTR, but that the effects of the eutectic/peritectic reaction during solidification and $\delta \rightarrow \gamma$ transformation behavior during subsequent cooling should be taken into consideration as one of the main roles of the narrow BTR in addition to the favorable effect of delta ferrite having a greater solubility of P and S than austenite.

4. Conclusions

This investigation was part of an effort to improve the cracking resistance of weld metal of SUS 310S fully austenitic stainless steel. Special emphasis was placed on the development of a fuller understanding of the effect of decreased P and S content on cracking resistance. From these investigations the following conclusions can be drawn:

- (1) SEM observation clearly indicated the presence of phosphides and sulphides at boundaries in commercial SUS (AISI) 310S melt run weld metal. Phosphides were identified as M_3P type highly enrich-

ed in Cr and P containing a considerable amount of Fe and a small amount of Ni. Sulphides were identified as $\alpha\text{-MnS}$ type highly enriched in Mn, Cr and S and depleted in Fe and Ni. However, in the exceptional case of a negligible content of Mn, sulphides predominantly enriched in Cr and S and depleted in Mn, Fe and Ni were only observed.

- (2) According to the result of SEM observation ($\times 10,000$) and EDX analyses, more sulphides were observed than phosphides in SUS 310S and SUS 304 melt run weld metals containing the equal levels of P and S contents as well as both sulphides and phosphides were formed in greater numbers in SUS 310S than in SUS 304. With regard to the limit of P and S content to form phosphides and sulphides, phosphides were not observed at the P content of not more than 0.006% in SUS 310S and less than 0.06% in SUS 304, while a small number of sulphides were detected even at the S content of 0.003-0.005% in both SUS 310S and SUS 304. However, as far as commercial SUS 310S with 0.021%P and 0.007%S is concerned, it was revealed that more phosphides were actually formed than sulphides due to the much higher P content than the S content.
- (3) The degree of crack susceptibility in weld metals of SUS 310S fully austenitic stainless steels was strongly dependent upon P, in particular, and S content, whereas C and Si appear to have a smaller effect but Mn and N may exert a little favorable influence. Hence, cracking decreased with reduced P and S content was reasonably correlated with a decrease in formation tendencies of phosphides and sulphides. The best cracking resistance was associated with the presence of undetectable amount of phosphides and negligible amount of sulphides, when the P and S content were below about 0.006% and below about 0.005%, respectively. From the practical point of view, it was confirmed in the weld metals of electron beam bead-on-plate welding that no horizontal cracks occurred in the weld metals of newly developed SUS 310S with 0.001%P and 0.003%S although commercial SUS 310S contained a number of cracks.
- (4) It was noted that, although a small number of phosphides and sulphides or sulphides formed in weld metals of SUS 304 containing approx. 0.12%P and 0.005%S or 0.025-0.056%P and 0.005-0.01%S, respectively, these types of SUS 304 weld metals were more resistant to cracking than SUS 310S modified with 0.001%P and 0.003%S, involving no phosphides and a smaller amount of sulphides. Consequently, superior crack resistance of SUS 304 was primarily interpreted in terms of the effects attributed to the eutectic/peritectic reaction at the com-

pletion of solidification and $\delta \rightarrow \gamma$ transformation behavior during subsequent cooling in addition to the effect of primary delta ferrite on the decrease in the segregation of P and S.

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