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

— Effect of La or REM Addition on Solidification Crack Resistance —

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Abstract

A series of studies has been performed with the primary objective of producing crack-free, fully austenitic stainless steel weld metals. Previous papers^{1),2)} indicated the reduction in P content in particular and S content below 0.005% each was one of the most beneficial means to reduce cracking susceptibility when the alloying elements were varied within the JIS composition range of SUS (AISI) 310S at present. Unfortunately it seems very difficult and costly to remove P by the conventional refining techniques. Therefore this investigation was undertaken to define an effective additive alloying element in promoting and improving the cracking resistance of SUS 310S containing a commercial level of P content. The qualitative effects of various alloying element additions on the solidification cracking resistance of SUS 310S with considerable levels of P and S content were preliminarily investigated by employing the Trans-Varestraint test. The result that a small amount of La was the most beneficial element in the composition range of fully austenitic microstructure was realized and subsequently was further confirmed with the cast-pin tear test and GTA (gas tungsten arc) bead-on-plate weld. Accordingly, commercially available SUS 310S plates to which La or partly REM (mish metal) was systematically added as an alloying element were made and subjected to the Trans-Varestraint test and other practical tests. It was revealed as a result that the optimum content of La or REM addition reduced cracking susceptibility to a large extent. The effects of La and REM additions were discussed in terms of the formation of sulphides and phosphides of high solidification temperature. This study resulted in the development of SUS 310S (25Cr-20Ni alloy) which exhibited excellent resistance to weld metal solidification cracking. In fact, for SUS 310S with the optimum levels of La or REM content it was proved with EB (electron beam) bead-on-plate welding that fully austenitic welds could be made which were free from horizontal cracks.

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

1. Introduction

Fully austenitic stainless steels, which provide excellent corrosion resistance and long-time stability in high temperature service, are subject to solidification cracking in single-run weld metals produced by gas tungsten arc (GTA) or electron beam (EB) welding process. Therefore, the programmed investigations have been metallurgically performed with the ultimate object of developing a fully austenitic stainless steel which would be highly resistant to weld metal cracking in practical production service. Studies were undertaken on SUS 310S (25Cr-20Ni steel corresponding to AISI 310S) as it is known to produce typical fully austenitic weld metals in melt-run welding. As a result the mechanisms and the chemical compositional causes of cracking in SUS 310S weld metal were first determined in the previous papers.^{3),4)} It has been shown that cracks take place predominantly by a solidification cracking mechanism in melt-run weld

metals³⁾. Especially, a better understanding of the harmful effect of P and S content on the cracking susceptibility was obtained on the basis of the fundamental investigation⁴⁾ of microsegregation or microconstituents enriched in P and/or S as well as the results of the Trans-Varestraint test and other hot cracking tests.^{1),2)} In other words, the cracking sensitivity was improved in its degree with a reduction in the content of P in particular and/or S; moreover, from the standpoints of the extreme decrease in the formation of phosphides and sulphides as well as the improvement in the cracking resistance of GTA and EB weld metals in practical use, it was recommended that the respective contents of P and S should be below 0.005%²⁾.

However, it is difficult to bring down P content to such a low level in austenitic stainless steels by conventional refining techniques used widely in Japan at present,^{5),6)} although the reduction in S content is reported to be relatively easy.⁷⁾ Hence, the use of

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high-purity raw materials with very low levels of P content from the beginning,⁶⁾ the special refining smelting techniques such as MSR method,⁸⁾ and so on, are particularly required to reduce the P content. The fact is that it involves a great cost disadvantage in addition to technological difficulty at present to yield austenitic stainless steels with extremely low levels of impurities such as P and S.

For these reasons another metallurgical procedure is taken into consideration that the deleterious effect of P and/or S is controlled by adding various profitable alloying elements to a commercial material. It would be very significant if the cracking susceptibility of SUS 310S weld metal containing a commercial level of P content could be improved in fully austenitic microstructure by this readily available procedure.

Much work has been done and a number of qualitative statements have appeared in the literature on the beneficial effects of various alloying element additions on weld cracking tendency. However, there are few papers in which the cracking susceptibility is determined quantitatively or systematically by means of the ductility curve or the BTR (solidification brittleness temperature range) and there is little information in relation to the beneficial effect of alloying addition on the elimination of the harmful influence of P, so that advantageous alloying additions and their effects are not necessarily elucidated completely in detail.

Therefore, this investigation was designed to find out the most promising alloying element in a fully austenitic weld metal and to establish firmly its quantitative effect on the improvement in cracking susceptibility of commercial SUS 310S. Mn, Ti, Zr, Nb (Cb), Ta, Mo and La (one element of mish metal (REM)), which were first selected as promising alloying elements according to the available data⁹⁾⁻¹⁹⁾ published up to the present, were individually added to SUS 310S with about 0.03%P and 0.05%S that was remarkably susceptible to solidification cracking. The plates containing various alloying contents were all subjected to the Trans-Varestraint test, and then based on this result the effect of each alloying element on cracking susceptibility was compared and evaluated quantitatively. It was consequently found that the plates and weld metals containing a small amount (less than 0.5%) of Ti, La, etc., showed a narrower BTR, which would lead to a greater resistance to cracking, in spite of a fully austenitic microstructure. The effect of Ti, La, etc. addition was further confirmed by using the modified cast-pin tear test (CPT test) and GTA spot and bead welding. It was concluded from these results that a

small amount of La was the most beneficial element.

On the basis of this conclusion three kinds of SUS 310S in the compositional range of about 0.017–0.025%P and 0.001–0.018%S to which various contents of La and REM were added were made and they were all subjected to the above-mentioned cracking tests and EBW as well to verify positively the beneficial effect on cracking resistance of SUS 310S containing a commercial level of P and S content. Consequently the optimum levels of La or REM content were found to be effective enough to prevent cracking in SUS 310S weld metals produced with GTAW or EBW. Moreover, the metallurgical effect of La and REM was discussed and interpreted in terms of the effect on the behavior of phosphide and sulphide.

2. Materials Used and Hot Cracking Tests

2.1 Selection of promising alloying element for improved cracking resistance

A considerable amount of literature has dealt with the effects of alloying elements on cracking susceptibility with the objective of obtaining a crack-resistant fully austenitic stainless steel weld metal. Hull⁹⁾ determined the effects of various elements on cracking of 16Cr–20Ni cast steel by means of the CPT test, and consequently stated that Cr, Mn, Ni and Mo decreased the susceptibility to hot cracking and that Si, Nb, Ti, C, Hf, Zr, and B caused increasing amounts of cracking. He suggested that if carbide stabilization is required, the addition of Ta should be preferred since both Ti and Nb increased the cracking susceptibility of steels. However, the P and S content in the steel used were extremely low levels of 0.0005–0.005 and 0.004–0.011%, respectively. Gueusier, et al.¹⁰⁾, investigated the cracking tendency in casting of 17Cr–13Ni steel with 0.015%P and 0.01%S and as a result of their studies suggested that 2–6%Mn, about 0.05%Ce and about 0.05%Mg had a slightly beneficial effect although Zr, Nb, Sb and Cu were harmful. Koizumi, et al.¹¹⁾, were successful in improving the cracking susceptibility of Inconel 600 by adding Ca instead of Mg during refining. Kazennov, et al.¹²⁾, evaluated cracking susceptibility of 16Cr–20Ni high purity steel (P, S and Si: 0.005% (each)) by the modified MVTU-LTP and indicated that the addition of Mo, W, Mn and Ce didn't impair cracking resistance and that alloying with Zr, B and Nb increased cracking tendency. Hoerl, et al.¹³⁾, pointed to Mn and C as potent cracking inhibitors from the results of the segmented circular-groove test of modified Type 347 weld metal (19Cr–13Ni–0.62–0.88Nb+Ta), showing

that increasing Mn and C content from 1.4 to 4% and from 0.076 to 1%, respectively, reduced cracking. Hasebe, et al.¹⁴⁾, reported that the cracking susceptibility in SUS 347 with less than 0.01%P and S was improved by adding Ta instead of Nb. Sadowski¹⁵⁾ indicated that the addition of 0.25%Ti and/or 0.01% REM (50%Ce, 27%La, 16%Nd, etc.) to 26Cr-17Ni steel weldments with 0.02%P and 0.015%S and that of about 3%Nb to 25Cr-20Ni steel GTAW weldments were effective to decrease the cracking tendency. Ohno, et al.¹⁶⁾, reported that increase in C content from 0.25 to 0.55 reduced the cracking susceptibility of 25Cr-20Ni steel with about 0.02%P and 0.01-0.02%S. Gooch, et al.^{17), 18)}, investigated the effect of alloying elements on the cracking susceptibility of Type 310S (25Cr-20Ni steel) and consequently recommended that C and Si should be below 0.1% and 0.3%, respectively, and the addition of 3-6%Mn, 2.5-3%Mo or 0.2%N should be desirable; besides the close control of welding procedures is likely to be required to obtain crack-free fully austenitic welds. Masumoto, et al.¹⁹⁾, reported that the effect of Zr or Ti was more beneficial than that of Mn in reducing cracking in 3.5%Ni steel weld metals.

All the above results are not a direct good guide to this study because it was ambiguous whether all of them were obtained in fully austenitic microstructure, but on due investigation of them, Mn, Ti, Zr, Nb, Ta, Mo, Ca, Ce, REM, C, N, etc. are individually noticed as promising alloying elements which would be efficient in reducing the cracking susceptibility of fully austenitic weld metals. These are well known as sulphide-formers,²⁰⁾ desulfurization agents, deoxidizers, carbide-stabilizers, solid-solution strengtheners and/or interstitial elements.⁹⁾ However, there are few experimental results which were examined in terms of potent elements to form phosphides or to raise the melting temperature of the eutectic compounds with austenite and M₃P phosphide. Therefore, we consulted the data²¹⁾⁻²³⁾ on the melting points of phosphides between alloying elements and P as well as the literature on the ternary diagram of Fe-P-X system.²⁴⁾⁻²⁶⁾ From the results, part of which are listed in Table 1, it is inferred that Ba, U, Ti, Th and REM such as Ce, La, Nd and Pr appear to be favorable. However, it is difficult to get U and Th. On the other hand, the effects of N and C were first investigated in the process of this study. Consequently, increasing N content up to around 0.2% had a neutral effect on the cracking susceptibility of commercial SUS 310S with about 0.02%P and 0.01%S,²⁷⁾ and besides Brooks²⁸⁾ reported that N was related to the cause of spatter, concavity

Table 1 Phosphide type and its melting point picked up from literature²¹⁾⁻²⁶⁾.

| System | X - P [†] | | Fe - P - X ^{**} | |
|--------|--------------------------------|-------------------------------------|--|---------------------------|
| | Element (X) | Phosphide type Melting point(°C) | Formation phase type | Reaction temperature (°C) |
| B | BP | 1130 (1700-2100) | | |
| Ba | Ba ₃ P ₂ | 3080 (3080-3200) | | |
| Be | Be ₃ P ₂ | (1700-2100) | | |
| Ce | CeP | (2100-2500) | | |
| La | LaP | (2100-2500) | | |
| Nd | NdP | 2500* (2100-2500) | | |
| Th | ThP _{0.76} | 2850* (2900-2990) | | |
| Pr | PrP | 2850* | | |
| Co | Co ₂ P | 1386 | | |
| Mn | MnP | 1147 | α Fe+(Fe, Mn) ₃ P | 1025-1050 |
| | Mn ₂ P | 1320 | γ Fe+(Fe, Mn) ₃ P | 1000-1025 |
| | Mn ₃ P | 1200, 1230 | | |
| Mo | MoP | 1400 (1700) | | |
| | Mo ₃ P | (1700-2100) | | |
| Nb | NbP | 1730 (1700-2100) | α Fe+FeNbP | 1303 |
| | | | α Fe+FeNbP+Fe ₂ Nb | 1295 |
| | | | α Fe+FeNbP+Fe ₃ P | 1045 |
| Re | ReP | 1200 | | |
| | Re ₂ P | (1700-2100) | | |
| Ta | TaP | 1660 (1700-2100) | | |
| Ti | TiP | 1580 (1700-2100) | α Fe+FeTiP | 1363 |
| | Ti ₃ P | (1700-2100) | α Fe+FeTiP+Fe ₂ Ti | 1330 |
| | | | α Fe+FeTiP+Fe ₃ P | 1047 |
| U | UP | (2610) | | |
| W | WP | 1450 (1700-2100) | α Fe+Fe ₃ W ₂ | 1110-1529 |
| | | | α Fe+Fe ₃ P | 1000-1050 |
| | | | α Fe+Fe ₃ P+WP | 970 |
| V | VP | 1320 (1700-2100) | α Fe+(Fe, V) ₃ P | 1030-1250 |
| | V ₃ P | (1700-2100) | | |
| Zr | ZrP | (1700-2100) | α Fe+FeZrP | 1325 |
| | | | γ Fe+FeZrP | 1295 |
| | | | γ Fe+FeZrP+Fe ₂ Zr | 1200 |
| | | | α Fe+Fe ₄ ZrP | 1240 |
| | | | α Fe+Fe ₄ ZrP+Fe ₃ P | 1040 |

†, (), * and ** are quoted from the literature (21)-(26)

and porosity in EB weld metal. The addition of 0.4-0.55%C proved to be very beneficial and this effect of C was attributed to the formation of a large number of eutectics with austenites and M₇C₃ carbides²⁹⁾ and increasing C content in the fully austenitic microstructure range seemed to be a little harmful instead. Moreover, it was difficult to add Ba, Ce, Nd, Pr and Ca in producing materials. Thus, the individual effect of C, N, Ba, Ce, Nd, Pr and Ca was not described in this paper although the effect of Ce, Nd or Pr was actually involved in that of REM. From these reasons, Mn, Ti, Zr, Nb, Ta, Mo and La and partly REM were selected as added elements in prospect, and these additive effects were investigated.

2.2 Sample preparation and materials used

Two kinds of commercial SUS 310S, the chemical compositions of which are given in Table 2, were chiefly used as base materials. A desired content of alloying addition was achieved by adding an aimed amount of high-purity alloying element to a base material.

Table 2 Chemical compositions of SUS 310S used chiefly as base materials

| Materials | Composition (wt%) | | | | | | |
|-----------|-------------------|-------|------|------|-------|-------|-------|
| | (SUS) | C | Si | Mn | P | S | Ni |
| 310S-F | | 0.08 | 1.0 | 1.2 | 0.03 | 0.05 | 19.5 |
| 310S-G | | 0.052 | 0.54 | 1.02 | 0.022 | 0.003 | 19.25 |

About 1 kg mixed material was prepared in a crucible and then melted by high-frequency induction melting in an Ar atmosphere after initial evacuation to 10^{-4} Torr vacuum. The molten material was cast at about 1450°C into 6 Cu molds to make 6 pins in the modified CPT test and into 2 Cu molds to produce plates ($100' \times 50'' \times 5'$ mm) used for the Trans-Varestraint test and GTAW. The chemical compositions of added elements of plates or cast-pins are shown in Table 3. Moreover, SUS 310S plates of 3 and 12 mm in thickness containing various contents of La or REM were produced by vacuum induction melting, forging at $1200 \sim 800^{\circ}\text{C}$, hot rolling at $1200 \sim 800^{\circ}\text{C}$ and solution treating at 1100°C for 1 hr to confirm the effect of La or REM further in the case of 0.02%P and 0.01%S. These chemical compositions are given in Table 4.

2.3 Hot cracking tests

2.3.1 The Trans-Varestraint test

The Trans-Varestraint test was conducted on the cast plates ($100' \times 50'' \times 5'$ mm) in Table 3 and the rolled plates ($100' \times 100'' \times 3'$ mm) in Table 4, when GTAW was performed under the welding conditions of 150A, 20V and 100 mm/min and 100A, 12.5V and 150 mm/min, respectively. 5 and 3 mm thick plates were tested at each level of the augmented strain of about 4% and 0.2, 2.5 and 3.75%, respectively. To evaluate the effect of alloying element addition on cracking susceptibility, the BTR, the details of which were described in the previous papers,^{29), 30)} was determined for each alloy.

2.3.2 Modified cast-pin tear test

The cast-pin tear test (CPT test), which was developed by Hull,^{31), 32)} was expected to be easily applicable to the study of the effect of alloying addition. In this study, modified CPT test whose cast-pins were larger in length and diameter than the originals³¹⁾ was

Table 3 Chemical compositions of SUS 310S containing various contents of alloying elements added intentionally.

| Group | Added element | Composition (wt%) | (thickness) |
|-------|---------------|---|-------------|
| I | (310S-I) | 0.08C-0.97Si-1.21Mn-0.028P-0.05S-24.38Cr-19.49Ni | (5 mm) |
| | Mn | (1)2.22 (2)3.23 (3)4.94 (4)6.45 | |
| | Ti | (1)0.05 (2)0.10 (3)0.14 (4)0.25 (5)0.48 (6)0.9 (7)1.4 (8)3.0 (9)5.0 | |
| | Zr | (1)0.10 (2)0.25 (3)0.41 (4)1.00 (5)1.50 (6)2.0 (7)3.15 (8)5.21 | |
| | Nb | (1)0.58 (2)1.05 (3)2.09 (4)3.10 | |
| | Ta | (1)0.57 (2)1.10 (3)2.01 (4)2.95 (5)4.0 (6)5.12 | |
| | Mo | (1)1.00 (2)1.48 (3)1.82 (4)2.68 (5)3.94 | |
| II | La | (1) 0.01 (2)0.012 (3)0.23 (4)0.28 | |
| | (310S-II) | 0.06C-0.68Si-1.10Mn-0.025P-0.015S-24.5Cr-19.5Ni | (5 mm) |
| III | La | (1)0.063 (2)0.20 (3)0.35 (5)0.70 | |
| | (310S-III) | 0.05C-0.50Si-1.00Mn-0.024P-0.002S-24.6Cr-19.3Ni | (5 mm) |
| IV | La | (1)0.035 (2)0.074 (3)0.15 (4)0.2 (5)0.28 (6)0.5 | |
| | (310S-IV) | 0.07C-0.52Si-0.80Mn-0.098P-0.003S-25.6Cr-19.9Ni | (5 mm) |
| IV | La | (1) 0.5 | |

Table 4 Chemical compositions of SUS 310S containing different contents of La or REM added intentionally.

| Materials (SUS) | Composition (wt%) | | | | | | | | thickness (mm) |
|-----------------|-------------------|------|------|-------|-------|------|------|-----------|----------------|
| | C | Si | Mn | P | S | Cr | Ni | La or REM | |
| 310S-0 | 0.070 | 0.61 | 1.05 | 0.021 | 0.011 | 25.8 | 20.1 | 0 | 3, 12 |
| 310S-G | 0.052 | 0.54 | 1.02 | 0.022 | 0.003 | 24.6 | 19.3 | 0 | 3, 12 |
| 310S-La 1 | 0.059 | 0.59 | 1.06 | 0.020 | 0.007 | 26.0 | 20.3 | 0.053 La | 3, 12 |
| 310S-La 2 | 0.072 | 0.56 | 0.92 | 0.018 | 0.005 | 22.8 | 18.4 | 0.145 La | 3, 12 |
| 310S-La 3 | 0.063 | 0.59 | 1.04 | 0.020 | 0.004 | 26.1 | 20.1 | 0.335 La | 3, 12 |
| 310S-REM 1 | 0.067 | 0.62 | 1.03 | 0.021 | 0.008 | 25.7 | 20.5 | 0.006 REM | 3, 12 |
| 310S-REM 2 | 0.058 | 0.62 | 1.03 | 0.021 | 0.007 | 25.9 | 20.3 | 0.072 REM | 3, 12 |
| 310S-REM 3 | 0.060 | 0.60 | 1.05 | 0.017 | 0.004 | 26.3 | 20.3 | 0.17 REM | 3, 12 |
| 310S-REM 4 | 0.066 | 0.60 | 1.04 | 0.020 | 0.002 | 26.1 | 20.3 | 0.21 REM | 3, 12 |

employed in consideration of horizontal cracks occurring in EB weld metals of thick plates because the application of EBW to thick plates is being realized and is more and more hopeful about the future. An example of the dimensions of the mold used is shown in Fig. 1, where the length of \textcircled{L} is varied at 100, 125 and 150 mm. The longer the restraint distance was, the more liable to occur crackings

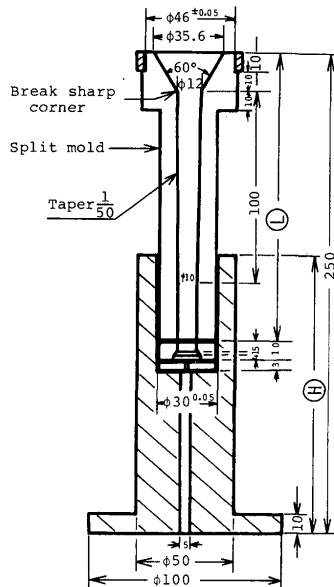


Fig. 1 Mold type for cast-pin tear test.

were.

Examples of a typical crack and its fracture surfaces in SUS 310S-I (0.14%Ti) cast-pin are shown in Fig. 2. Crack surfaces in (c) and (d) demonstrate the features of Type D, D-F and F of a solidification crack.³³⁾ It was revealed from the results of SEM observation as indicated in Fig. 2 that cracks in cast-pins were solidification cracks.³³⁾ At room temperature after casting the cast-pin was examined for surface cracks with a stereobinocular microscope at a magnification of about 15 times, and the length of the cracks on the pin surface was measured. The cracking susceptibility was evaluated by the ratio of the total crack length to the circumferential length: Cracking ratio $C_R = (l_c / 35) \times 100$ (%). Cracks were always circumferential and in extremely rare cases they resulted in the separation of the cast-pin into two parts. When the cast-pin was separated or the total crack length (l_c) was greater than 35, C_R was expressed as 100%.

2.3.3 Gas tungsten arc welding and electron beam welding test

A GTA welding was utilized on $100^l \times 50^w \times 5^t$ mm plates or partly on $100^l \times 50^w \times 12^t$ mm plates to melt a spot under the condition of 300A, 20V and 2 sec or to produce a weld bead under the condition of 250A, 20V and 700 or 1400 mm/min. The length of cracks

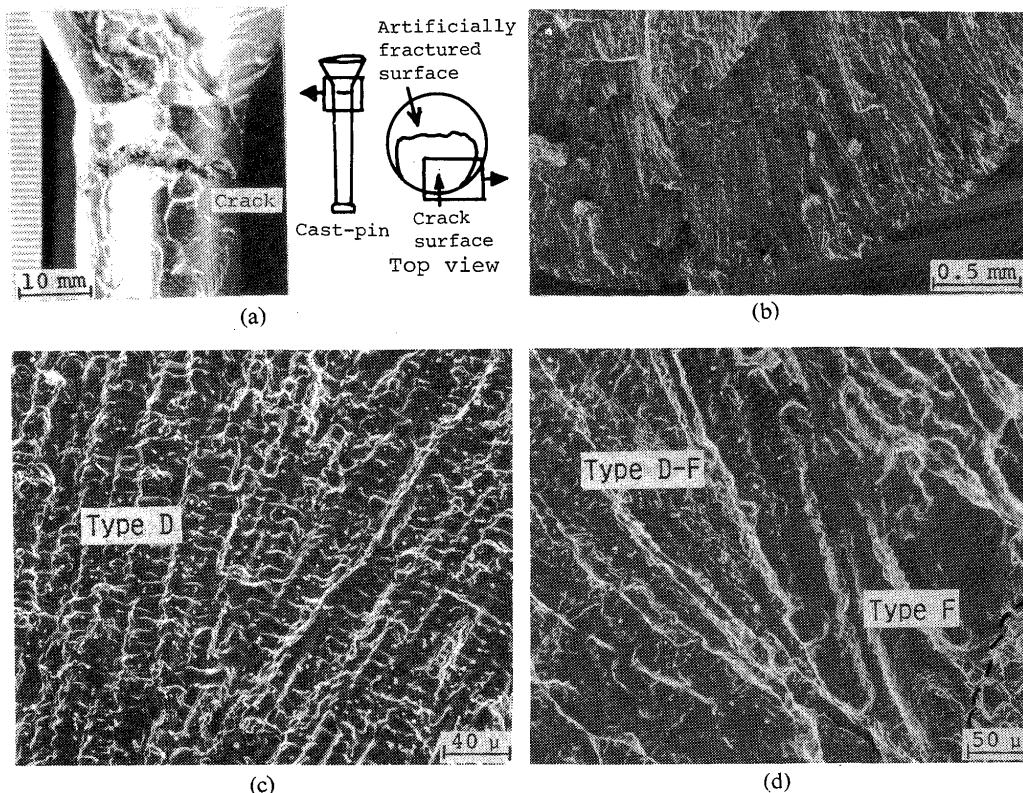


Fig. 2 Typical crack and its fracture surfaces in SUS 310S-I (0.14%Ti) cast-pin: (a) crack in cast-pin; (b), (c), (d) SEM micrographs of crack surfaces, showing characteristics of solidification cracking.

on a nugget surface or a bead surface was measured, and the total crack length per one nugget or one bead obtained by taking the average of 4 nuggets or 2 beads was used as the assessment of cracking susceptibility.

Moreover, an EB welding was conducted on 12 mm plates in Table 4 under the condition of 30 or 40 mA, 150 kV, 1000 or 1500 mm/min and $a_0=1.0$ to confirm the beneficial effect of La or REM on the reduction in cracking in practical use. After welding, samples were sectioned and examined for horizontal cracking. The length of cracks observed in three cross-sectional weld metals was measured with a light microscope at $\times 100$ magnification and the total crack length per one cross section was used as the assessment of cracking susceptibility.

3. Results and Discussion

3.1 Effects of alloying element additions on cracking susceptibility of SUS 310S with considerable amount of P and S

3.1.1 Effect of alloying elements on BTR

Cast plates ($100^l \times 50^w \times 5^t$ mm) in Table 3 were subjected to the Trans-Varestraint test to determine the effects of Mn, Ti, Zr, Nb (Cb), Ta, Mo and La on the BTR of SUS 310S (P: 0.028%, S: 0.05%) which is rarely used commercially as a rod of good machinability in spite of being out of the JIS (Japan Industrial Standard) compositions and is liable to suffer from the great problem of solidification cracking. This type of SUS 310S was first selected to demonstrate the effect of each alloying element more remarkably. Figure 3 shows the relationship between each alloying

element content and the BTR at the augmented-strain of 4%. The BTR of SUS 310S as a base was about 320°C and was marked X at the composition of 0% (and about 1.2% in the case of Mn only). For Ti and Zr addition at about 0.5% the BTR was decreased to about 200°C. Increasing La content up to 0.01–0.3% reduced the BTR down to 180–120°C. For Ta, Nb, Mo and Mn the BTR was gradually decreased in its degree as the added content of each element was increased in the chemical composition ranges of more than 0.5, 1, 2 and 3%, respectively. Consequently the BTR of less than 230°C was achieved by the additions of about 0.01–0.3%La, 0.1–1.2%Ti, 0.2–0.8%Zr, 2.5–5%Ta, 2.5%Nb, 4%Mo and 6.5%Mn. It was suggested in the previous paper that the BTR of less than 110°C was required to produce the crack-resistant, fully austenitic weld metal of SUS 310S in practical use. No alloying element can achieve this necessary condition of the BTR but it is noted that La is the most powerful in reducing the BTR of SUS 310S containing a considerable level of P and S.

3.1.2 Investigation of solidification structures and selection of beneficial alloying elements

The main aim of this study is to discover the most beneficial alloying element that would make fully austenitic weld metal lest susceptible to cracking. Therefore, the microstructures of SUS 310S with various alloying elements added were first observed by the light and the scanning electron microscope (SEM) and then secondary phases or inclusions were investigated by the X-ray diffractometer (XD) and the

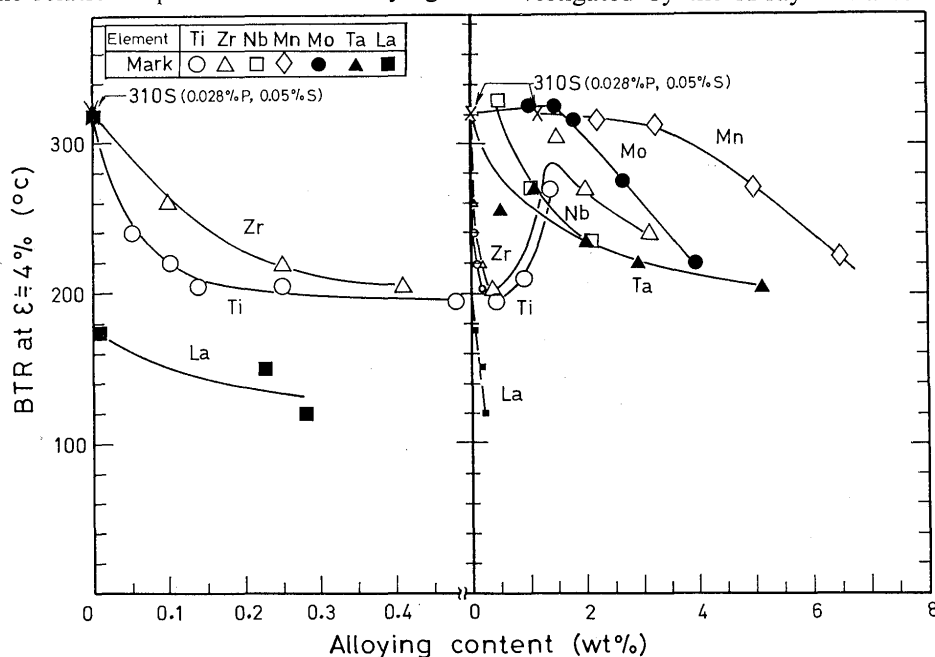


Fig. 3 Effects of Ti, Zr, Nb, Mn, Mo, Ta and La content on BTR at $\varepsilon=4\%$ of SUS 310S-I (about 0.028%P, 0.05%S) weld metal.

energy dispersive X-ray spectrometer (EDX) method and the ferrite indicator. Thermal analyses were made on the alloys to determine the liquidus, the solidus and/or the eutectic temperature. These results are summarized in **Table 5**. An example of microstructure in the case of 5%Ta addition is shown in **Fig. 4**, indicating that a large amount of austenite-TaC eutectic formed along columnar grain and cellular dendritic boundaries. Such eutectic products formed in the case of more than 0.5%Ta, Nb and Zr and more than 1%Ti. On the other hand, in the case of 0.7–1.5%Ti, 1–3%Zr and 1.5–4%Mo residual delta ferrite of about 0.1–1% was detected by ferrite indicator and the delta ferrite phase was seen in a thin long shape by SEM observation. The presence of delta ferrite of

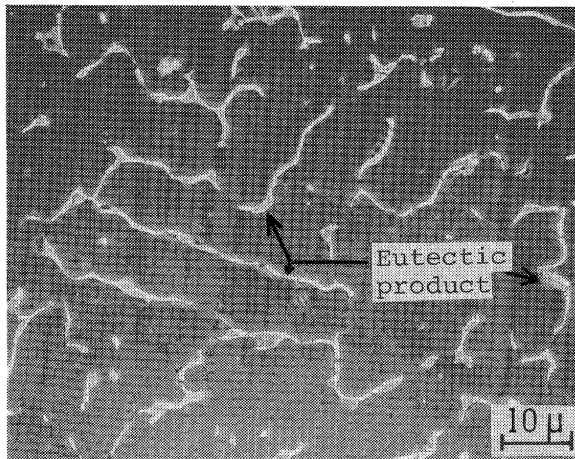


Fig. 4 SEM microstructure of SUS 310S-I containing about 5%Ta, showing eutectic products in cell and grain boundaries.

more than 1% was experienced at more than 1.5%Ti and more than 3%Zr. Therefore, it is understood by comparison of the result in **Fig. 3** with the result in **Table 5** that a considerable reduction in the BTR was closely associated with the formation of delta ferrite or a large amount of eutectic products. Consequently fully austenitic weld metals were yielded in the case of Ti of below 0.5%, Zr of about 0.2 or less, La of less than 0.3%, Mo of about 1% or less and Mn of less than 7%.

Subsequently, the additive effect of a small content of Ti, Zr, La or Mo under the conditions of fully austenitic microstructure was confirmed by conducting the modified CPT test and GTA bead and spot welding. (However, the effect of Mn on the cracking susceptibility was not investigated in the following in this paper because it was reported to be beneficial at the level of 2–6%Mn at about 0.01%S¹⁸⁾ and to be neutral at approximately 0.004%S in reference to SUS 310S with about 0.02%P^{27), 29)} and Gooch, et al.¹⁸⁾, indicated that an increase in Mn content had a deleterious effect on corrosion resistance of Type 310S under moderately oxidizing conditions.) These results are plotted against the BTR in **Fig. 5**. It is found from this figure that the minimum BTR could be achieved in fully austenitic SUS 310S (about 0.03%P and 0.05%S) was about 120, 195, 260 or 320°C by the addition of La, Ti, Zr or Mo, respectively. Moreover, it is apparent that the cracking susceptibility i.e. the total crack length L_T and the cracking ratio C_R in practical cracking tests decreased accordingly with a reduction in the BTR

Table 5 Summary of main secondary phases or eutectic products formed and solidus or eutectic temperature in the case of Mn, Ti, Zr, Nb, Ta, Mo and La added to SUS 310S-F.

| Added element (wt%) | | Secondary phase or eutectic product | Solidus temperature(TS) or eutectic temperature(TE)(°C) |
|---------------------|----------|--|---|
| Mn | 1~7 | (MnS) | (TS) 1,330 (3%Mn)~1,300 (5%Mn) |
| Ti | 0.5 | (TiS) | (TS) 1,325 (0.5%Ti) |
| | 1~5 | δ , γ -TiC | (TE) 1,160~1,155 (5%Ti) |
| Zr | 0.25~0.5 | (ZrC) | |
| | 1~5 | δ , γ -ZrC | (TE) 1,235~1,230 (3%Zr) |
| Nb | 0.5~5 | γ -(Fe,Cr,Ni) ₂ Nb, γ -NbC | (TE) 1,275~1,270; 1,240~1,235 (3%Nb) |
| Ta | 0.5~5 | γ -TaC | (TE) 1,270~1,265 (5%Ta) |
| Mo | 1.5~4 | δ | (TS) 1,340 (TE) 1,310 (4%Mo) |
| La | ~0.3 | (LaP) | (TS) 1,335 (0.3%La) |

although plotted points are appreciably scattered—the La addition made L_T in a nugget decrease from 28 mm to less than 5 mm and rendered C_R reduce from 100 to 50%, and particularly GTA bead welds with La added were possessed of the BTR of 180°C or less and were crack-free. Meanwhile, judging synthetically from the above results, the effect of Ti, Zr or Mo addition was insufficient in preventing cracking and La was confirmed to be the most beneficial to the

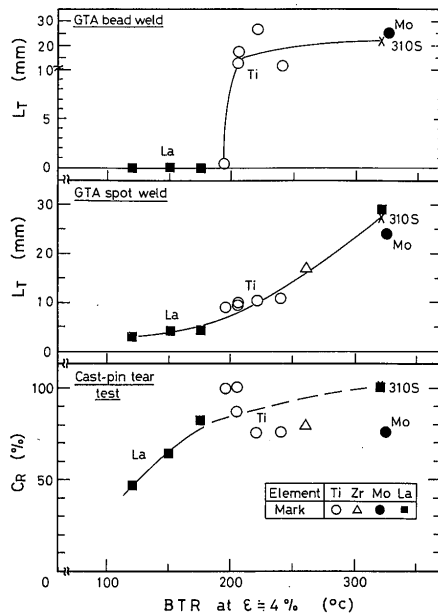


Fig. 5 Relationship between BTR at $\varepsilon = 4\%$ of weld metals and cracking susceptibility of cast and weld metals for SUS 310S containing a small amount of Ti, Zr, Mo and La.

improvement of the cracking susceptibility of SUS 310S containing a considerable amount of P and S.

3.2 Effect of La or REM on improved cracking resistance of commercial SUS 310S

3.2.1 Effect of La or REM on BTR

On the basis of the results of the preliminary tests in 3.1 the additive remedy of La or REM (mish metal involving La) for cracking susceptibility was further investigated by employing commercially available SUS 310S containing about 0.02–0.025%P and 0.002–0.015%S. Figure 6 shows the relationship between La or REM content and the BTR obtained at $\varepsilon = 4$ or 3.8% by the Trans-Varestraint test. It is apparent that the BTR was decreased with an increase in La or REM content up to a certain fixed content between about 0.07 and 0.3% and above it the BTR decreased was increased conversely. The optimum additive content, which actually exists according to the S content, is about 0.08%La for 0.001–0.002%S, about 0.14%La or REM for 0.002–0.011%S and about 0.3%La for 0.015–0.02%S. In addition, the content required to obtain the BTR of less than 130°C whose value was associated with the property of crack-free GTA spot weld metal of SUS 310S containing decreased P and S content as reported in the previous paper²⁾ is 0.03–0.15%La for less than 0.002%S, 0.04–0.4%La or 0.05–0.25%REM for 0.002–0.007%S and 0.17–0.45%La for 0.015%S.

Next, the effect of La on the solidification ductility

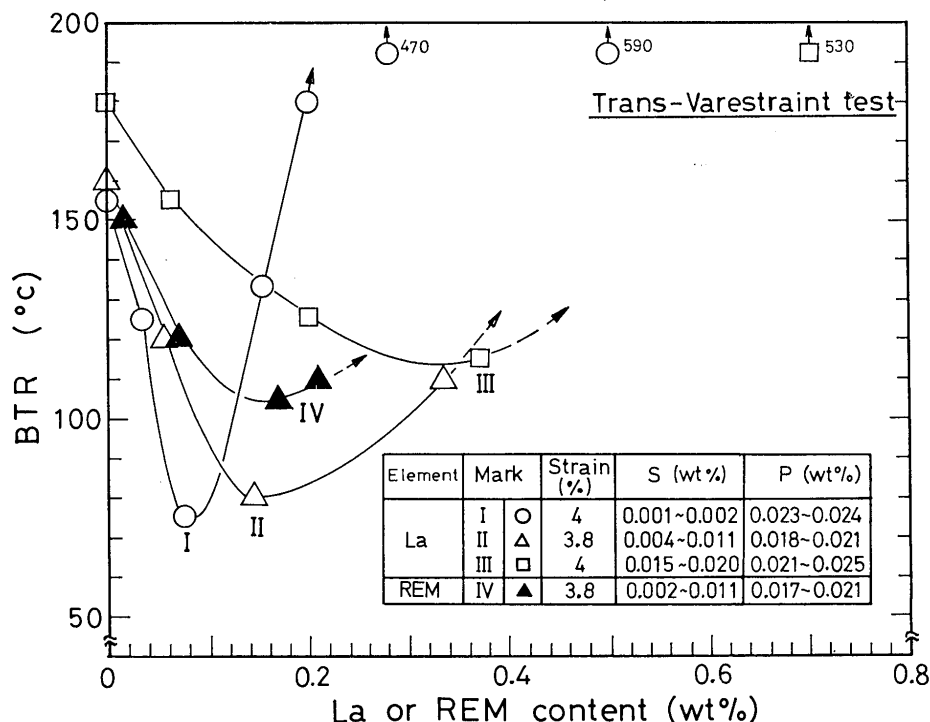


Fig. 6 Effect of La or REM content on BTR at $\varepsilon = 3.8\text{--}4\%$ of SUS 310S weld metals containing varied S contents (P: 0.017–0.025%).

curve was investigated by the Trans-Varestraint test. The result is shown in Fig. 7(a), together with that of SUS 304 containing about 0.027%P and 0.010%S, and in addition the ductility curves for SUS 310S improved with the decrease in P in particular and/or S content are shown for reference in Fig. 7(b). According to Fig. 7(a), the BTR distinctly decreased in the order of 0, 0.05, 0.34 and 0.15%La at any augmented-strain from 0.2 to 3.8%, and thereby the CST value (the critical strain rate for a temperature drop) increased. In the case of 0.15%La the BTR at $\epsilon=2.5-3.8\%$ was exceedingly reduced to about 70–80°C, which is equivalent to that of modified SUS 310S for P and S content decreased to about 0.001 and 0.003% and for P, S, Si and C content decreased to about 0.002, 0.003, less than 0.01, 0.014–0.016%, respectively, as stated in the previous papers.^{1),2)} However, the reduced BTR at low augmented-strain and the $B\epsilon_{min}$ (the minimum augmented-strain required to cause cracking) were wider and lower, respectively, than those of SUS 304, which is under-

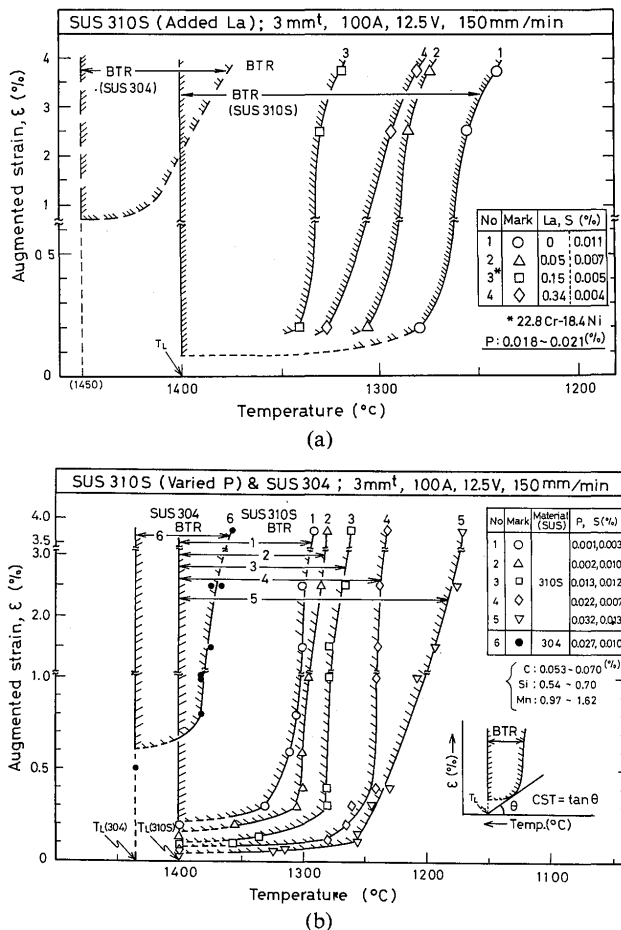


Fig. 7 Solidification ductility curves for SUS 310S weld metals with La added (a) and with P and/or S decreased (b) in contrast to that for commercial SUS 304 weld metal, showing effects of La addition and decrease in P and/or S on reduction of BTR.

stood in terms of the difference in the solidification process between SUS 310S and SUS 304 as stated in the previous paper.^{2),34)} Moreover, based on the result of SUS 310S with REM added it was found that the property of the solidification ductility curve was improved in its degree in the order of the addition of 0.006, 0.07, and 0.21 and/or 0.17%REM.

3.2.2 Investigation of cracking susceptibility by practical cracking tests

The modified CPT test and simple cracking tests by GTA spot and bead welding were performed on SUS 310S plates given in Tables 3 and 4 to confirm whether or not the optimum contents are effective to the improvement of cracking susceptibility in practical weld service. These results are given in Figs. 8 and 9. In the case of 0.002%S, it can be noted that no cracks were observed at the La additions of about 0.06–0.15% although cracks of about 2 and 2.5 mm in total length and of 65% in cracking ratio were present at 0%La, while cracking susceptibility was enhanced on the contrary at La contents in excess of about 0.25%. In the case of about 0.015%S, 0.35–0.4%La decreased C_R from 100 to 5%, 0.2–0.4%La decreased L_T from 4

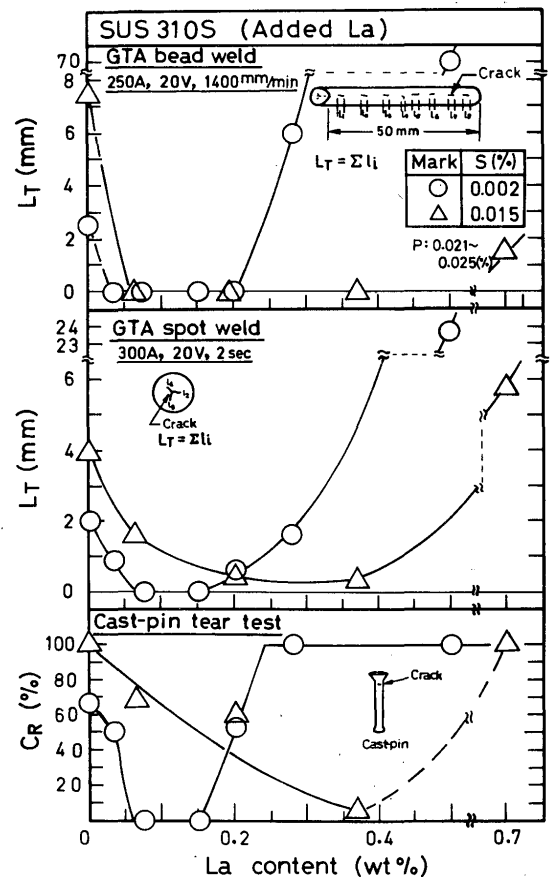


Fig. 8 Effect of La content on C_R in cast-pin tear test and L_T in GTA spot and bead welds for SUS 310S (P: 0.025%, S: 0.002 and 0.015%).

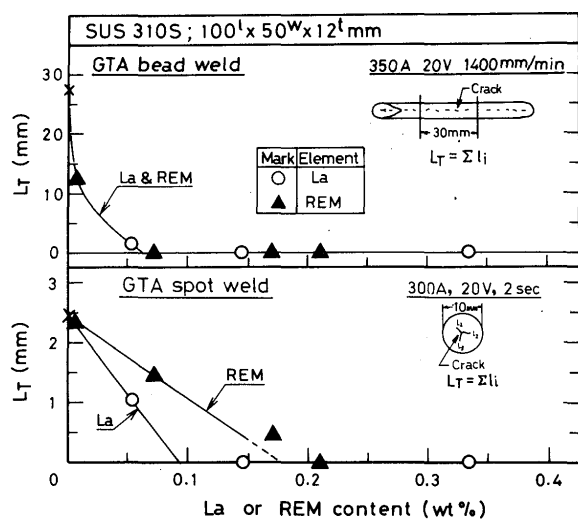


Fig. 9 Effect of La or REM content on L_T in GTA spot and bead welds for SUS 310S.

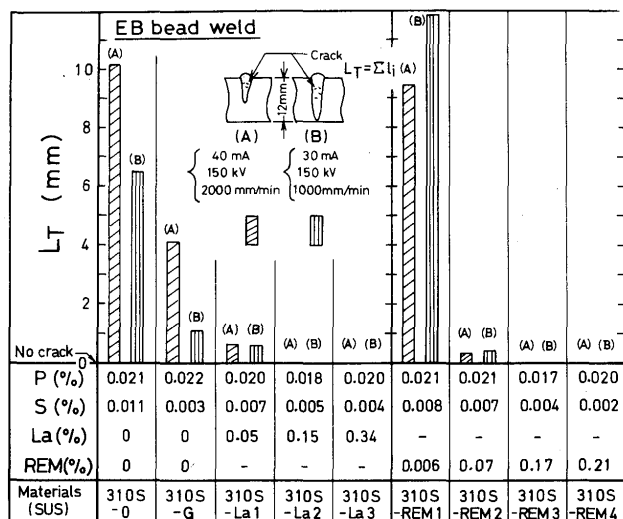


Fig. 10 Effect of La or REM content on L_T in cross section of electron beam weld metals of SUS 310S.

to less than 0.5 mm in GTA spot welds, and La content being between 0.06 and 0.4% eliminated cracking in GTA melt-run beads. Moreover, in the case of 0.003–0.011% S, in spot welding the cracks of $L_T=2.5$ mm occurred in a nugget without La or REM addition but cracks were not formed at about 0.09–0.35% La or 0.21% REM, and in bead welding L_T had a tendency to decrease with La or REM content and consequently no cracks were observed at more than 0.07% La or REM content though the cracks of $L_T=27$ mm were present with no La or REM. Furthermore, EB bead-on-plate welding was conducted on SUS 310S containing La or REM content in Table 4. The result is shown graphically in Fig. 10, in which L_T of horizontal cracks in one cross section of EB weld metals is compared at each content under two welding conditions. It is virtually noted that the S content of base material was removed from 0.011 to about 0.002% with an

increase in La or REM content from 0% to 0.34 or 0.21%, and that a decrease in S content from 0.011 to 0.003% decreased horizontal cracking. Nevertheless it is still worthier of notice that EB weld metals with 0.15 and 0.34% La or 0.17 and 0.21% REM were sound without cracks.

From the above results of practical tests, it was verified that the addition of a small amount of La or REM is exceedingly beneficial to the improvement of the cracking susceptibility of commercial SUS 310S. Moreover, it was found that the optimum content and reduced cracking susceptibility mainly varied according to the S content in the case of about 0.02–0.025% P:—the recommendable content of La or REM is 0.06–0.15% for less than 0.003% S, 0.09–0.35% for 0.003–0.013% S and 0.2–0.4% for 0.013–0.02% S.

3.2.3 Metallurgical investigation of the effect of La or REM addition in reducing cracking susceptibility

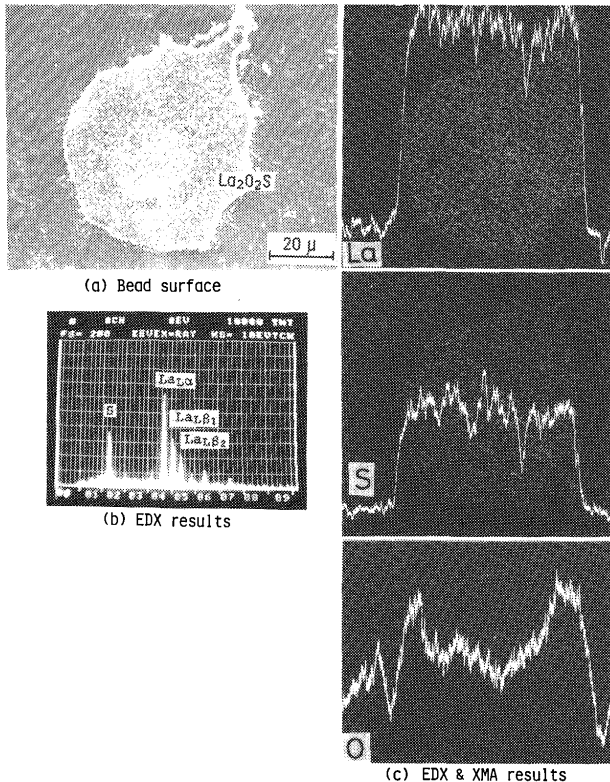
The reason why the optimum La addition significantly caused the BTR to decrease to a considerably small value and was effective to the reduction in cracking susceptibility in practical tests was metallurgically investigated. Since La is well known to be a potent desulfurization-agent and deoxidizer,³⁵⁾ the chemical compositions of S and O and, for reference, P and N were analyzed for base metals and GTA weld metals (250A, 20V and 100 mm/min) of SUS 310S containing various La and S contents to examine whether the desulfurization reaction, deoxidation reaction, etc. would take place in steelmaking and during welding. The chemical analysis results are given in Table 6. From the analytical result of materials in group I which were made by adding to the base alloy with 0.03% P and 0.05% S, it is clearly understood that S and O were easily removed through the addition of La during melting. Moreover, from the result of materials in group II, which were produced so as to contain approximately constant levels of S and O on the basis of the above result, it was revealed that S and O in weld metals were also eliminated by La addition, and it appeared from the comparison of group II and III that the degree was more remarkable for the elimination with an increase in the S and O content in base metals. It is thought from these results that desulfurization and deoxidation reaction take place in the case of a considerable content of S and O during welding as well as during melting and casting. However, it cannot be judged that dephosphorization reaction would occur during welding.

On the one hand, a large amount of slag was observed on the bead surface of the GTA weld metal

Table 6 Chemical analyses of La, P, S, O and N in base metals and weld metals in the case of SUS 310S containing various La and S contents.

| | La (wt%) | | P (wt%) | | S (wt%) | | O (ppm) | | N (ppm) | |
|-----|---------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| | Aimed content | Base metal | Base metal | Weld metal | Base metal | Weld metal | Base metal | Weld metal | Base metal | Weld metal |
| I | 0 | 0 | 0.028 | | 0.050 | | 83 | | 374 | |
| | 0.3 | 0.012 | 0.023 | | 0.002 | | 7 | | 319 | |
| | 0.5 | 0.23 | 0.021 | | 0.007 | | 30 | | 336 | |
| | 1.0 | 0.28 | 0.022 | | 0.001 | | 22 | | 320 | |
| II | 0 | 0 | 0.025 | 0.026 | 0.015 | 0.017 | 60 | 45 | 219 | 228 |
| | 0.1 | 0.063 | 0.021 | 0.024 | 0.014 | 0.011 | 67 | 15 | 238 | 209 |
| | 0.3 | 0.2 | 0.024 | 0.023 | 0.018 | 0.012 | 73 | 12 | 227 | 197 |
| | 0.5 | 0.35 | 0.023 | 0.024 | 0.015 | 0.010 | 61 | 25 | 239 | 226 |
| III | 0 | 0 | 0.024 | 0.024 | 0.002 | 0.002 | 70 | 58 | 140 | 130 |
| | 0.2 | 0.15 | 0.024 | 0.025 | 0.001 | 0.001 | 19 | 14 | 130 | 134 |
| | 0.3 | 0.2 | 0.023 | 0.024 | 0.001 | 0.001 | 11 | 12 | 148 | 131 |
| | 1.0 | 0.5 | 0.024 | 0.023 | 0.001 | 0.001 | 16 | 17 | 133 | 138 |

with La added. Therefore SEM, EDX, XMA (X-ray microanalysis spectrometer) and ED were used to observe microstructure of the slag, to analyze the constituent elements and to determine the structure type or to identify the nature. The results of the slag on the bead surface of SUS 310S containing 0.023%P,

**Fig. 11** SEM micrograph (a) and EDX and XMA result of slag (b), (c) on SUS 310S-II (La: 0.35%) weld bead surface, showing enrichment of La, S and O in slag.

0.015%S and 0.35%La are shown as an example in **Figs. 11** and **12**. It is obvious from such results that the majority of the slag on weld bead with La added was $\text{La}_2\text{O}_2\text{S}$ and part of it was La_2O_3 . Moreover, the both results of ED (electron diffraction method) through TEM (transmission electron microscope) and EDX through SEM using carbon-extraction replicas indicated that $\text{La}_2\text{O}_2\text{S}$, La_2O_3 and LaS were the components of the slag.

Then, the mechanism of desulfurization and deoxidation were discussed from a thermodynamic point of view. An example of thermodynamic data,³⁶⁾ melting points³⁷⁾ and gravity^{37), 38)} are summarized in **Table 7**. It is immediately predicted in terms of thermodynamic data that $\text{La}_2\text{O}_2\text{S}$ and La_2O_3 are easy to form, which is in good accord with the analytical results of the slag. It is concluded from all the above results that the desulfurization and the deoxidation reaction occur during welding and are attributed to

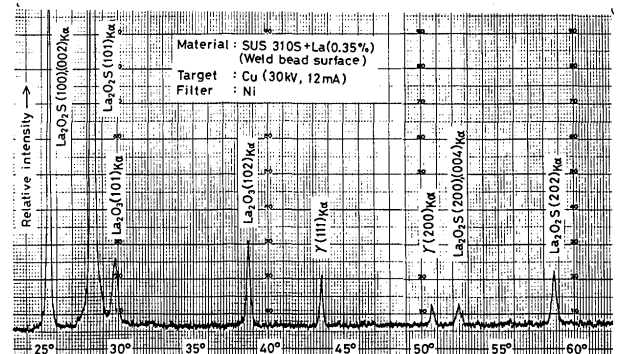
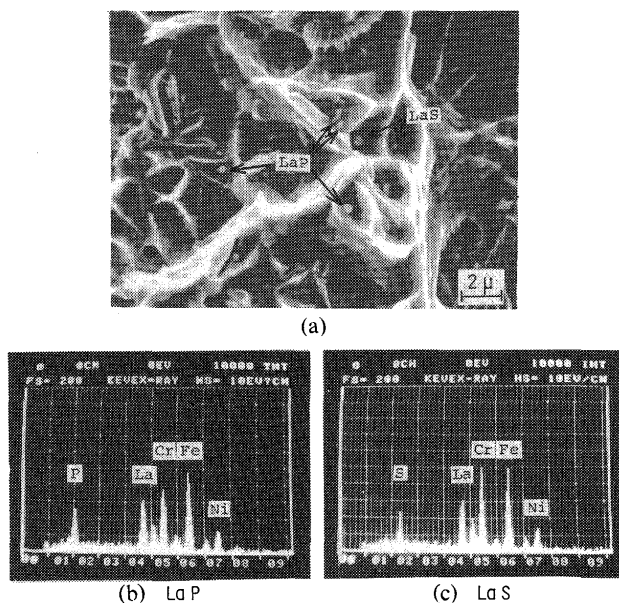
**Fig. 12** X-ray diffraction result on bead surface of SUS 310S-II (La: 0.35%).

Table 7 Summary of standard free energies of formation (ΔG°), equilibrium constants at 1700K (K_{1700K}), melting points ($^\circ\text{C}$) and gravity for La compounds in steelmaking.

| | Reaction | ΔG° (kcal) | K_{1700K} | Melting point ($^\circ\text{C}$) | gravity |
|-----|---|-------------------------|----------------------|--|---|
| (1) | $\text{La} + \text{S} = \text{LaS}$ | 48 | 1.6×10^6 | $\begin{matrix} 1970 \\ (2200) \\ (2300) \end{matrix}$ | $\begin{matrix} 5.7 \\ (5.75) \end{matrix}$ |
| (2) | $2\text{La} + 2\text{O} + \text{S} = \text{La}_2\text{O}_2\text{S}$ | 198 | 3.0×10^{25} | 1940 | 5.77 |
| (3) | $2\text{La} + 3\text{O} = \text{La}_2\text{O}_3$ | 208 | 5.7×10^{26} | $\begin{matrix} 2210 \\ (2300) \end{matrix}$ | 6.56 |

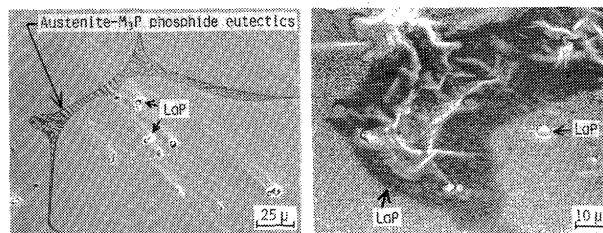
the formation of the slag such as $\text{La}_2\text{O}_2\text{S}$ and La_2O_3 .

On the other hand, inclusions or microconstituents in base metals and weld metals were investigated. **Figure 13(a)** shows the SEM micrograph of artificially fractured surface of weld metal with 0.018%P, 0.005%S and 0.15%La. The surface in (a) is characteristic of ductile fracture mode and in the center of dimples globular and granular inclusions can be seen. EDX results, which are given in Fig. 13(b) and (c), showed these inclusions to be enriched in La and P or La and S with respect to the matrix. The analytical results of inclusions through extraction replica films confirmed that the inclusions were identified as LaP type phosphides and LaS type sulphides which were both depleted to little or no extent in Cr, Fe, Ni, Mn, etc. Furthermore, it was sometimes observed in the base metals with about 0.015%S and added La that $\text{La}_2\text{O}_2\text{S}$ or La_2O_3 as slag was caught in a cluster in the matrix. According to the above observation results, it was

**Fig. 13** SEM micrograph of artificially fractured surface of SUS 310S-La2 (P: 0.018%, S: 0.005%, La: 0.15%) weld metal and EDX results (b), (c) of inclusions in (a), showing formation of inclusions enriched in La and P, and La and S, respectively.

qualitatively found that LaP phosphides were chiefly present in weld metals but there were few LaS sulphides.

Subsequently, LaP phosphides were in particular investigated concerning whether and to what extent the solidification temperature of LaP phosphides was enhanced compared to that of austenite- M_3P eutectic products. The melting temperatures of SUS 310S type sample containing about 0.5%P and a certain content of La were determined through a hot-stage microscope. **Figure 14** (a) and (b) show SEM micrographs of the sample before heating and after heating up to 1150 $^\circ\text{C}$. In (a), LaP phosphides or sometimes the phases enriched in La, P and O were predominantly formed in the globular or granular shape in the matrix although austenite- M_3P eutectic products were in the film-like form at the grain boundaries. It is readily supposed from this observation that LaP phosphides would solidify at higher temperatures than the solidification temperature of austenite- M_3P eutectics. Figure 14(b) demonstrates that LaP phosphides didn't melt at about 1150 $^\circ\text{C}$, while austenite- M_3P eutectics melted at about 1070–1100 $^\circ\text{C}$. Moreover, the melting temperature of LaP was investigated by using the samples (about 10 \times 10 mm) containing about 0.024%P, 0.018%S and 0.2%La, and 0.023%P, 0.001%S and 0.2%La with the one side fractured artificially. The thermocouples were attached to the surface on this side. Then samples were subjected to the thermal cycle at the heating rate of the order of 800 $^\circ\text{C}/\text{min}$ in an argon

**Fig. 14** SEM microstructures of SUS 310S type cast with 0.5%P and La added, showing melting of M_3P type phosphides but no liquation of LaP type phosphides at 1150 $^\circ\text{C}$: (a) before heating and (b) after heating to 1150 $^\circ\text{C}$.

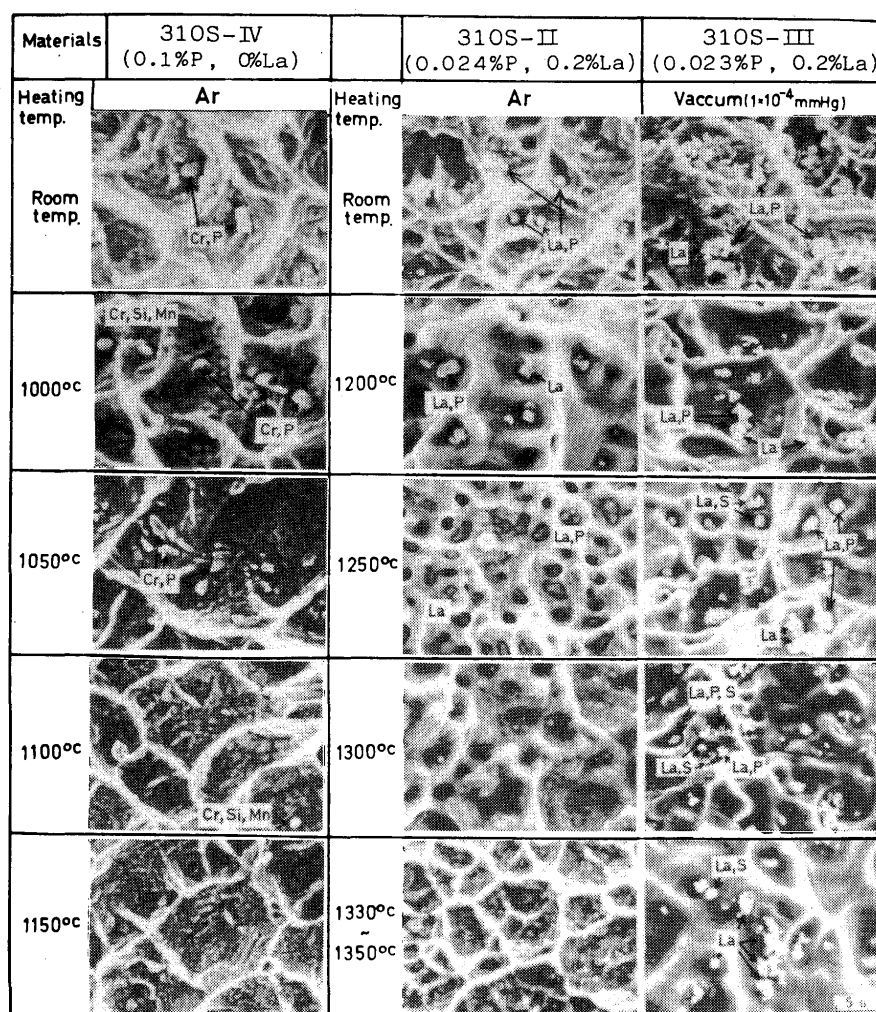


Fig. 15 SEM micrographs of artificially fractured surfaces of 310S-II-La (2) (0.024%P, 0.2%La), 310S-III-La (4) (0.023%P, 0.2%La) and for reference 310S-IV (0.1%P, 0%La) at room temperature before heating and after heating to various peak temperatures in temperature range 1000–1350°C.

atmosphere or in a vacuum of 10^{-4} Torr. **Figure 15** shows the SEM micrographs of fracture surface before and after heating up to any preselected maximum temperature of about 1000 to 1350°C. An example of M_3P phosphide in SUS 310-P2 with about 0.1%P and without La is compared for reference. According to this example, a large number of inclusions (austenite- M_3P) enriched in Cr, P, etc. in the center of dimples melted away at more than 1100°C, which agrees with the other experimental results²⁹⁾ and the supposition. On the other hand, for the sample with La addition it was observed that LaP phosphides were present below 1250°C and markedly decreased in number above 1300°C. Furthermore, La_2O_3S and LaS were observed to be present over 1350°C. It is therefore judged that the melting point of LaP phosphides was not higher than that of LaS sulphides or La_2O_3S oxysulphides but that it could be raised by about 150–200°C through La addition, which duly implies the reduction in the BTR.

To confirm further the beneficial effect of La on the reduction in the harmful influence of P, SUS 310-P2 (about 0.1%P) plates ($100^l \times 50^w \times 5^t$ mm) without La addition and with approximately 0.5%La added were subjected to the Trans-Varestraint test at $\epsilon = 4\%$. The result, as shown in **Fig. 16(a)** and (b), indicated that the La addition caused the maximum crack length (L_M) to reduce from 5.6 to 0.57 mm. The L_M of 0.57 mm corresponds to the BTR of about 90°C. It is consequently noted that the dramatic decrease in the BTR and the great improvement of cracking susceptibility actually resulted in SUS 310S type weld metals with La added, and the beneficial effect of La is primarily ascribed to the rise in the solidification temperature of phosphides due to the formation of LaP type phosphides.

On the other hand, for an excess of La addition the BTR broadened as the lower temperature limit of the BTR fell on the contrary. The reason was further investigated. **Figure 17(a)** and (b) presents the

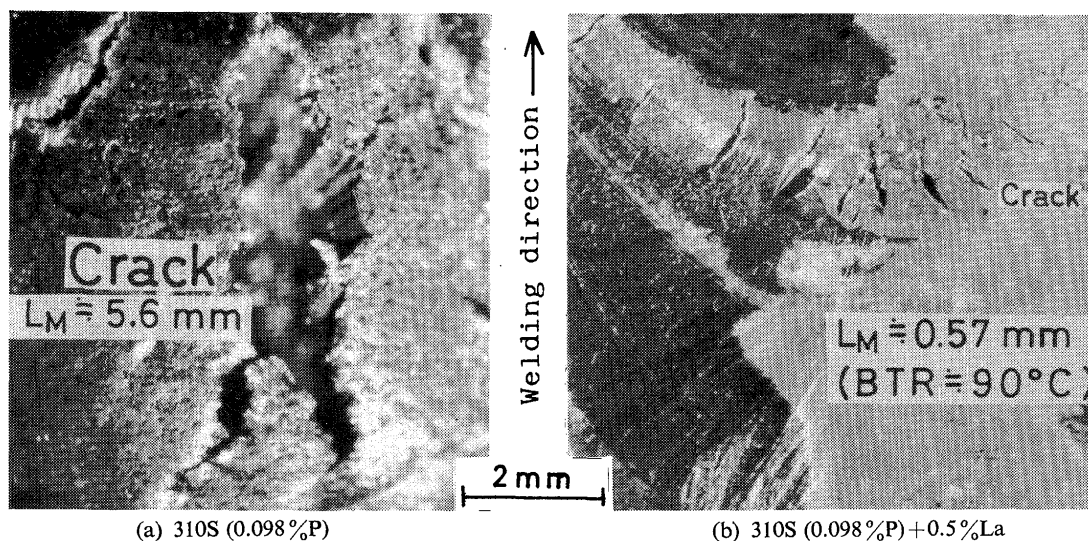


Fig. 16 Bead surface appearance of (a) 310S with 0.1%P and (b) 310S with 0.1%P and 0.5%La subjected to Trans-Varestraint test at $\varepsilon = 4\%$, showing extreme difference in crack length, which results in improvement in harmful influence of P due to La addition.

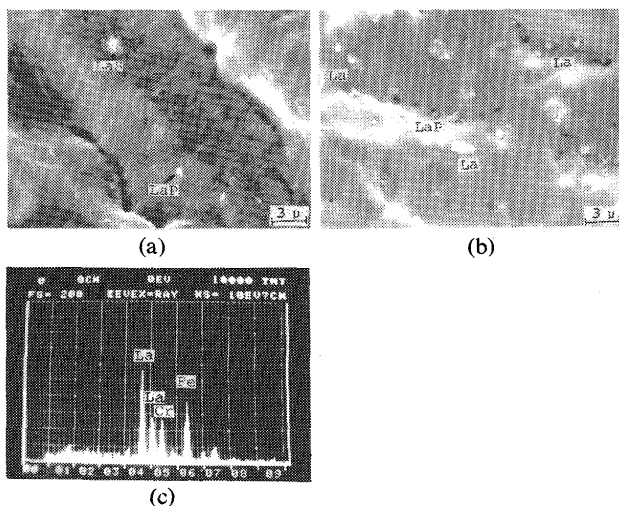


Fig. 17 SEM micrographs of solidification crack surfaces in SUS 310S-La2 (0.15%La) (a) and SUS 310S-La3 (0.35%La) (b) weld metal after Trans-Varestraint test and EDX result (c) of inclusion in (b), demonstrating formation of larger number of inclusions enriched in La in SUS 310S-La3.

fracture surfaces of solidification cracks in 310S-La2 (0.15%La) and 310S-La3 (0.34%La) weld metal, respectively. In (b) inclusions enriched in La, an example of the EDX result of which is given in Fig. 17 (c), were recognized to increase in number suddenly. In the case of both 0.001%S-0.7%La and 0.019%S-0.5%La the lower temperature limit of the BTR was about 810 and 870°C, respectively. Moreover, according to the binary diagrams of Fe-La^{38), 40)} and Cr-La,⁴⁰⁾ La-Fe eutectic and La-Cr eutectic exist in the La-rich composition side of about 95%La at the eutectic reaction temperature of $780 \pm 5^\circ\text{C}$ and about 900°C , respectively. From a comparison between

the lower temperature limit of the BTR and the eutectic reaction temperature of La and Fe or Cr, inclusions enriched in La in weld metals for an excess of La are judged to be a low melting La-austenite eutectic, and it is taken for granted that the increase in the formation of such eutectic products resulted in the wider BTR and the enhanced cracking susceptibility. This evidently suggests that the optimum levels of La addition exist to improve cracking resistance.

Therefore, a formula to predict the optimum levels of La addition was roughly examined in consideration of main inclusions formed by La addition. Thus the optimum La content is given by the content first to remove S as $\text{La}_2\text{O}_3\text{S}$ of higher melting point and then by the content to remove P as LaP as follows:

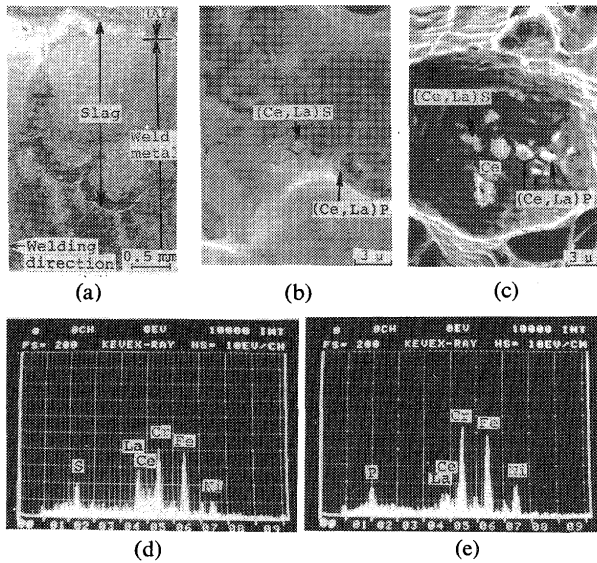
$$\text{La} = 4.5\text{P} + 8.7\text{S} \quad (1)$$

where the symbol of each element represents the concentration in wt%. The optimum contents of La obtained by the experiments such as the Trans-Varestraint test, etc. and by the equation (1) are tabulated in Table 8. By comparison the equation (1) is regarded to be very useful.

Subsequently the effect of REM was investigated. Figure 18 (a), (b) and (c) are SEM micrographs of bead surface, solidification crack surface and artificially fractured surface, respectively, in weld metal of 310S-REM4 (0.02%P-0.002%S-0.21%REM) and Figure 18 (d) and (e) are an example of the EDX results of the slag on the bead surface and inclusions in weld metal. It is revealed from these results that $(\text{Ce}, \text{La})_2\text{O}_3\text{S}$ principally formed on the bead surface and $(\text{Ce}, \text{La})\text{P}$ formed in weld metal and on the solidification crack

Table 8 Comparison of recommended optimum La content given by experiments (Trans-Varestraint test, etc.) and formula (1) in respective levels of P, S and O.

| | S, P, O (wt %) | Optimum La (wt%) | La given by formula(7.1) (wt%) |
|-----|-------------------|------------------|--------------------------------|
| I | 0.001–0.024–0.015 | 0.06–0.15 (0.1) | 0.12 |
| II | 0.005–0.020–0.025 | 0.09–0.24 (0.15) | 0.13 |
| III | 0.016–0.024–0.006 | 0.17–0.4 (0.3) | 0.25 |

**Fig. 18** SEM micrographs of SUS 310S-REM4 (0.02%P, 0.002%S, 0.21%REM) weld metal and EDX results, showing formation of slag enriched in Ce, La and S and inclusions enriched in Ce, La and P: (a) weld bead surface; (b) solidification crack surface; (c) artificially fractured surface; (d) EDX result of slag on bead surface in (a); (e) EDX result of inclusion in (c).

surface. Therefore, the effect and the behavior of REM are considered to be almost equivalent to those of La, so that the use of the cheaper REM can be recommended instead of La. La appeared to be easier to be added, however.

From all the above discussions in 3.2.3, it is summarized as follows: the main reason La was beneficial to narrow the BTR and to reduce the cracking susceptibility was attributed to the action that La raised the solidification temperature of phosphides above 1250–1300°C through the formation of LaP in the shape of granules and globules. Moreover, based upon the actions that La has a greater tendency to combine with S as $\text{La}_2\text{O}_3\text{S}$ or partly LaS and that an excess of La forms a low melting La-rich eutectic, the presence of the optimum levels of La addition was understood necessarily, which is true of REM, too.

4. Conclusions

The quantitative effects of various alloying elements, especially La, on the cracking resistance were in-

vestigated by using SUS 310S (25Cr–20Ni) containing commercial levels of P content for the objective of producing crack-free, fully austenitic weld metals. From these investigations the following conclusions were drawn:

1) For commercial SUS 310S with about 0.03%P and 0.05%S, the addition of 0.1–1.2%Ti, 0.2–0.8%Zr, 2.5%Ta or Nb, 4%Mo, about 6.5%Mn, or 0.01–0.3%La decreased the BTR from 320 to less than 230°C. In the case of some contents of Ta, Nb and Zr or Ti and Mo, however, the reduced cracking susceptibility was associated with the presence of austenite-carbide eutectics or delta-ferrite. Therefore, when the microstructure of weld metals was limited to a fully austenitic one, the addition of about 0.3%La, 0.5%Ti, 6%Mn and 0.1%Zr could decrease the BTR to about 120, 195, 230 and 260°C, respectively. Based on the results of practical cracking tests as well as the BTR, a small amount of La was regarded as the most beneficial element to reduce cracking.

2) The effect of La or REM on the improvement of cracking resistance was further investigated on commercial SUS 310S containing about 0.02–0.025%P and 0.001–0.02%S by employing the Trans-Varestraint test and the cracking tests with GTAW and EBW. It was again confirmed as a result that the optimum levels of La or REM were extremely effective to reduce the cracking susceptibility. It was furthermore verified that these optimum levels were beneficial enough to prevent horizontal cracking in EB weld metals of SUS 310S plates of 12 mm in thickness.

3) On the basis of the results of the metallurgical investigation as to why La or REM addition improved cracking resistance, it was revealed that La was remarkable for desulfurization agency and moreover that La could raise the solidification temperatures of MnS type sulphides and M_3P type phosphides to a great extent through the formation of $\text{La}_2\text{O}_3\text{S}$ type oxysulphides or LaS type sulphides and LaP type phosphides. REM instead of La was considered to have equivalently advantageous effects. It was inferred that these actions of La and REM were main reasons of the reduction in the BTR and consequently the

decrease in the cracking susceptibility in weld metals. On the other hand, an excess of La content was judged to be deleterious to cracking on the contrary, the cause of which was attributed to an increase in the number of low melting La-rich eutectics.

4) The optimum levels of La addition were obtained in the rough estimation in the following equation:

$$\text{La} = 4.5\text{P} + 8.7\text{S}$$

For commercial SUS 310S with about 0.02–0.025%P and less than 0.01%S in practical use the optimum La content was about 0.1–0.2%, which was consistent with the cracking susceptibility decreased strikingly in GTA and EB weld metals i.e. crack-free weld metals being the objective of this investigation.

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