



New Fluxes of Improved Weld Metal Toughness for HSLA Steels

SAW fluxes reduce Ti and B oxides, giving Ti and B microalloying additions that provide good toughness and crack opening displacement in 500-600 MPa (72.5-87 ksi) steels intended for arctic grade structures

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ABSTRACT. Weld metals which are microalloyed with Ti and B can show excellent properties even at low temperature. However, welding consumables which can consistently add optimum amounts of Ti and B to weld metal were relatively unknown. Therefore, new TiO_2 - B_2O_3 bearing fluxes, which can add Ti and B to weld metal by reduction of their oxides in the fluxes, were developed.

When TiO_2 was a main component, it was necessary to substitute BaO, MgO or some other basic component for CaO in order to eliminate the precipitation of perovskite ($CaTiO_3$) and have a good weldability. The new fluxes were shown to be able to consistently microalloy weld metals with optimum amounts of Ti and B (about 0.02% and 0.0045%, respectively).

Fracture appearance transition temperature of the weld metals was sufficiently low and only slightly deteriorated with the addition of Nb in the as-welded metal.

The new fluxes were successfully applied to the welding of node cans of offshore platforms, a sea berth, LPG tanks and ships.

Introduction

There is a large and growing demand in the arctic regions for large welded structures, such as offshore platforms, which require steel and joints to be highly reliable for operating at low temperatures. When submerged arc welding (SAW) techniques are applied in their construction, a highly basic flux with alloyed electrodes is usually selected as a welding consumable and a low level

welding heat input is usually selected to get satisfactory toughness of the welded joints. The alloying elements in weld metal, however, lead to tensile strength higher than actually needed.

Suzuki, Mori and others (Ref. 1) have pointed out that, in the SAW process, the simultaneous addition of Ti and B to weld metals beneficially improves their notch toughness. Since then, it has been recognized that the Ti-B can be used as microalloys to control the microstructure of ferritic steel welds, and Garland and Kirkwood (Ref. 2) have proved that their addition is essential to assure good mechanical properties.

Following Suzuki's lead, many researchers have studied and developed techniques to add Ti and B to ferritic steel weld metals. It was found that electrodes containing Ti and B produce these difficulties:

1. A large fluctuation of Ti and B content in weld metals affected by compositions of base metal plates.
2. High potential for cracking during production of electrodes.
3. Unstable yielding of Ti and B during steel production.

When the ferroalloys of these elements were present in agglomerated fluxes, the Ti and B content in weld

metals was not consistent enough. In retrospect, these techniques may not be appropriate for the addition of Ti and B to the weld metal because they are added through a reactive welding arc cavity.

Recognizing the benefits of microalloying weld metals with Ti and B, new fluxes were developed to have the following characteristics:

1. Good weldability, such as slag detachability and arc stability.
2. Optimum amounts of both Ti and B with as low oxygen and nitrogen contents as possible.

Weld metals were expected to obtain Ti and B by the reduction of TiO_2 and B_2O_3 contained in the fluxes occurring around the arc cavity. It was conceivable that the oxygen content in weld metals might be reduced if the stable oxide, TiO_2 , was substituted for SiO_2 —Fig. 1.

When weld metals are microalloyed with Ti and B, they have an optimum composition range for obtaining good toughness. Therefore, the composition of fluxes that affects Ti and B content in weld metal was studied.

Experimental Procedure

Flux Preparation

This research focused mainly on fused type fluxes produced by fusing a mixture of intended amounts of finely powdered materials in either 7 or 100 kg (15.4 or 220 lb) quantities. The 7 kg (15.4 lb) mixture was electrically fused for 30 minutes (min) using carbon electrodes in a water-cooled pan, after which the melt was poured into a large water pool to

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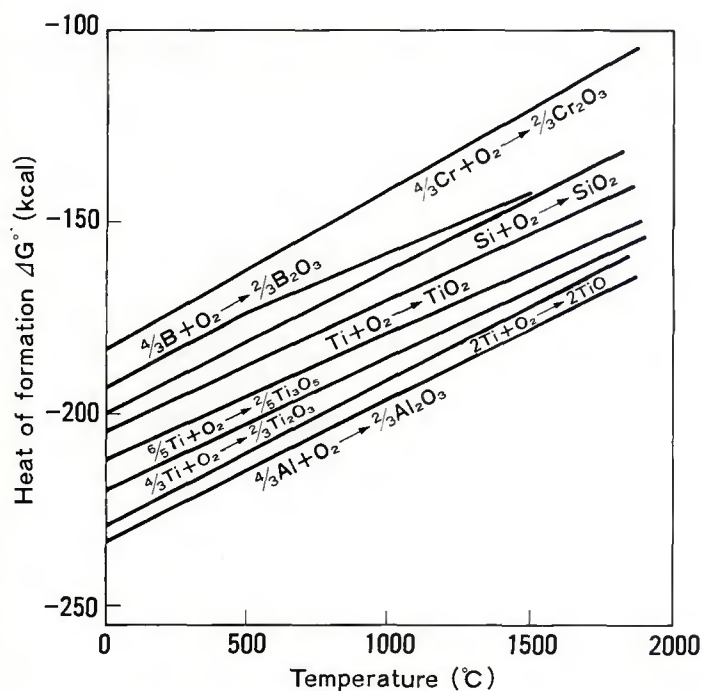


Fig. 1—Heat of formation for some oxides

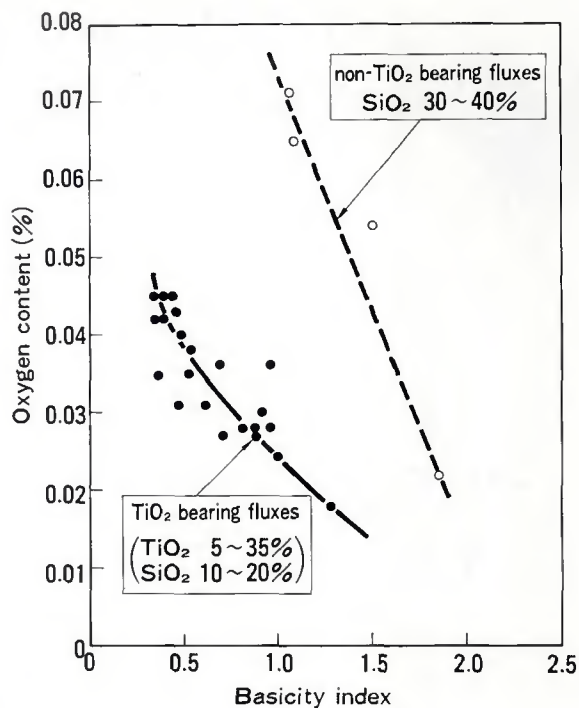


Fig. 2—Relation between the basicity index and the oxygen content in weld metals

granulate. Then, the granulated flux was dried, crushed, sieved, and baked at 300°C (572°F) for an hour (h) before its use. The 100 kg (220 lb) mixture was fused in a 100 kg (220 lb) fire brick-lined furnace before the granulation procedure and was used when large amounts of flux were necessary.

Welding Conditions and Mechanical Tests

An AC tandem welding machine with a Scott connection was used. Beads initially were welded on mild steel plates to examine the weldability of various fluxes. After a rough design of flux composition became clear, high strength low alloyed (HSLA) low temperature grade steel test panels were used. Each was 20 mm thick, 300 mm wide and 800 mm (0.79 × 11.8 × 31.5 in.) long with double V groove weld preparation. The chemical composition of these panels was 0.09% C, 0.28% Si, 1.40% Mn, 0.29% Ni, 0.11% V, 0.042% Nb, 0.035% Al and 0.0068% N.

Welding heat input was 40 kJ/cm (102 kJ/in.). After welding, slag detachability and bead shape were observed. Two sets of Charpy V-notch (Cv) test bars, weld sections and chips for chemical analysis were sectioned from the HSLA test panels. One set of Cv test bars was side-notched 6 mm (0.24 in.) thick and taken from the reheated weld metal region that had been affected by the weld thermal cycle of the following pass. The other set consisted of full size Cv test bars taken from the as-welded metal region.

A multipass weld was deposited in the single V-groove using a backing plate and

a 16 mm (0.63 in.) root opening for examining all deposit weld metals. An AC single electrode system was applied with a heat input of 31 kJ/cm (79 kJ/in.). Cv test bars, tension test pieces, weld sections, and chips for chemical analysis were sectioned from these test panels. Cv test bar notch positions were selected on the center and quarter lines of the bead width. The former were used to test the reheated weld metal region, and the latter were used to test the as-welded metal region.

Hot Cracking Susceptibility

When the hot cracking susceptibility of B₂O₃ bearing fluxes was examined, 16 mm (0.63 in.) deep single V-grooves with a groove angle of 60 deg were prepared on 36 mm (1.42 in.) thick plate. A single bead was welded in the V-groove with an AC single electrode welding machine; hot cracks in weld beads were then examined using dye penetrant testing and radiography.

Arc Stability

Arc stability in flux welding was unclear. For this reason it was necessary to measure it using the definition that "the welding arc is stable when reignition voltage and timing in the arc cycle are consistently stable."

The arc voltage of each electrode was measured with an adaptor. The adaptor consisted of two bridge-type full wave rectifier circuits, which had a common input terminal. One output terminal was crossed with a capacitor, and the other remained open. The former provided a

semi-quantitative reignition voltage; the latter provided an average voltage of arc as it appeared on voltage-meter on the control panel of the welding machine.

Results and Discussion

Flux Design

Initially, TiO₂-CaO-CaF₂Al₂O₃ fluxes containing no SiO₂ were used. The slag of this system did not vitrify and did not completely detach itself from the weld bead. An x-ray diffraction apparatus was used to examine the interface region of the slags. Those not completely detached were shown to consist of high amounts of perovskite (CaTiO₃). Perovskite's 1916–1970°C (3481–3578°F) equilibrium melting point is so high that it probably first precipitates and then attaches itself to the weld bead. Thus, SiO₂ was determined to be necessary for slags to vitrify. However, since oxygen content in weld metals increases with the SiO₂ content in fluxes, one requirement for the fluxes to have a vitrified slag of excellent weldability was that they should contain TiO₂ as one of main components and have as little SiO₂ as possible.

Welding slag detachability is improved when the thermal expansion coefficient largely differs from that of the steels and when the slags do not crystallize and detach themselves from the weld bead surface (Ref. 3). Therefore, one of the most important problems in using the flux containing TiO₂ was to eliminate the formation of perovskite in slags. When CaO content in fluxes was less than 10%, the slags were found to detach themselves from weld beads.

A region where slags attached themselves to weld beads corresponded with the perovskite precipitating area in the CaO-SiO₂-TiO₂ ternary system (Ref. 4). Therefore, other basic components, such as BaO and MgO were substituted for CaO. Trial fused fluxes of TiO₂-BaO-CaO-CaF₂-Al₂O₃-SiO₂ (A system) seemed to give much better weldability than those of TiO₂-MgO-CaO-CaF₂-Al₂O₃-SiO₂; for this reason, our efforts concentrated on the A system fluxes.

We also determined that fluxes which contained equiweight of BaO and TiO₂ were able to give good slag detachability. This can be explained by use of BaO-TiO₂ and BaTiO₃-CaTiO₃ phase diagrams (Ref. 4). The region of perovskite precipitation disappears when BaTiO₃ content is more than 80 mole-%, while the BaO-TiO₂ system has a eutectic point when BaO and TiO₂ are nearly the same weight. This also confirms that fluxes having similar eutectic composition have good weldability.

Slag detachability became noticeably better when Al₂O₃ content increased, which might be caused by the unusual thermal behavior of alumina-titanate at nearly 500°C (932°F) (Ref. 5). The highest applicable welding current also increased with Al₂O₃ content.

Oxygen and Nitrogen Content in Weld Metal

Oxygen content was some 0.04% and 0.02% when the basicity index was 0.5 and 1.3 respectively, with A system fluxes of TiO₂ content ranging from 5% to 35% and SiO₂ content ranging from 10% to 20%. Fluxes which did not contain TiO₂, showed an oxygen content of 0.065% at the basicity index† of 1.25 and 0.02% at the basicity index of 2.

The A system fluxes clearly give less oxygen content than that of fluxes which do not contain TiO₂, given the same basicity index—Fig. 2. When the basicity index is replaced with the IIW index‡, the difference in the oxygen content of weld metals only slightly decreased. The basicity indices were not applicable for these fluxes, if the indices are intended to predict oxygen content in weld metals.

Arc stability of the A system fluxes was not as good as that of commonly available SiO₂-CaO-MgO type flux. Therefore, alkali metal oxides were added to stabilize the arc—namely, arc reignition peak voltage. The trail electrode was affected more than the lead electrode—

†In this paper, the basicity index is defined as:

$$(0.108 \cdot \text{CaO} + 0.068 \cdot \text{MnO} + 0.10 \cdot \text{MgO} + 0.078 \cdot \text{CaF}_2 + 0.10 \cdot \text{BaO}) \div (0.105 \cdot \text{SiO}_2 + 0.002 \cdot \text{Al}_2\text{O}_3 + 0.08 \cdot \text{TiO}_2)$$

$$\ddagger \text{Bi} = (\text{CaO} + \text{CaF}_2 + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O} + \frac{1}{2}(\text{MnO} + \text{FeO})) \div (\text{SiO}_2 + \frac{1}{2}(\text{Al}_2\text{O}_3 + \text{TiO} + \text{ZrO}_2))$$

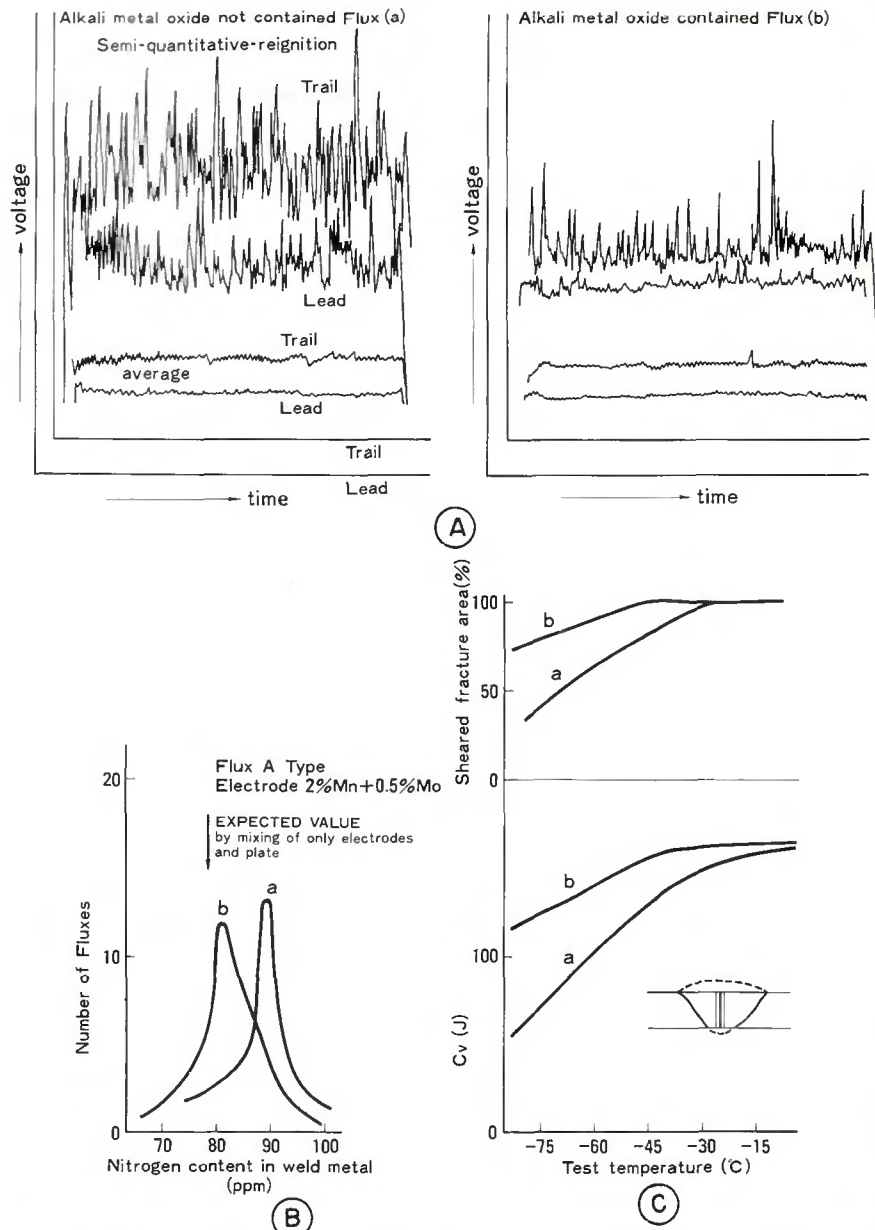


Fig. 3—Effect of alkali metal oxide in fluxes on: A—arc stability; B—weld metal nitrogen; C—Cv toughness

Fig. 3A.

With the stabilization of the welding arc, nitrogen content in the weld metal decreased by an amount nearly the same as that of the absorbed content; this was defined as the difference between the measured N content in the weld metal and the expected N content calculated from the nitrogen content of the base metal, electrodes, and average dilution of the base metal—Fig. 3B.

Ti and B Content in Weld Metal

The effect of flux composition on the reduction ratio of TiO₂ was also studied where the reduction ratio was defined as a ratio of the total Ti content in the weld metal to the TiO₂ content of the slags. The reduction ratio increased with increased Al₂O₃ content in the flux and

with an increased basicity index—Fig. 4.

The reduction ratio for A type fluxes was about 0.001; these contained 30% Al₂O₃ and had a basicity index of 1.0. The Ti content in the weld metal remained at approximately 0.020 ~ 0.025% when changing the welding parameters as follows: current from 400 to 800 amperes (A), voltage from 25 to 40 volts (V), and welding speed from 5 to 11.7 mm/s (11.8 to 27.6 ipm) for A system fluxes.

B in the weld metal was successfully added by reduction of B₂O₃ in fluxes and proportionally increased by increasing B₂O₃ content in them. The partition coefficient did not change when fluxes belonged to the same flux system. The partition coefficient (B^{weld metal}/B₂O₃^{flux}) was 0.009 for the A type fluxes—Fig. 5A.

The content of Ti and B in each bead

Regression coefficients were more than 0.91. It was clearly shown that B content in weld metal did not significantly affect tensile strength (Ref. 13).

Applications

Developed $TiO_2-B_2O_3$ bearing fluxes can be used to build the node cans of offshore platforms, LPG tanks, ships, and line pipes.

Node Cans of Offshore Platform

BS4360-50D class steel, which is 63 mm ($2\frac{1}{2}$ in.) thick, is used for offshore platforms. The chemical composition of such a plate was 0.14% C, 0.46% Si, 1.41% Mn, 0.006% P, 0.002% S, 0.023% Al, 0.03% Nb, 0.05% V and 0.0056% N. The plate was prepared with a double V-groove weld and was welded with the new A type flux #151 using a heat input of about 45 kJ/cm (114 kJ/in.). Some weld joints were given stress relief heat treatment at 630°C (1166°F) for 2½ hours (h) after welding.

Cv, tensile strength, and crack opening displacement (COD) tests were performed as well as analysis of the weld metal. Side-notched Cv test bars were cut from root areas and from sub-surface areas where the center axis of the test bar coincided with the quarter thickness line from the surface. The tension test pieces were taken both from the root

and from the sub-surface. The axis of the test pieces were set along the weld bead direction. Full size COD test pieces were cut according to British Standard DD-19, and notches were located to cross the axis of weld metal.

The chemical composition of the weld metals was 0.09% C, 0.26% Si, 1.3–1.5% Mn, 0.025% V, 0.010% Nb, 0.021% Ti, 0.0060% B, 0.0040% N and 0.025% O.

The tensile strengths were about 585 MPa (84.8 ksi) for as-welded metal and were about 570 MPa (82.7 ksi) for stress-relief heat treated weld metal. Average Cv absorption energy was not less than 110 J for as-welded metals and not less than 70 J for stress-relieved weld metal even at -60°C (-76°F)—Fig. 11A. The root areas showed slightly lower Cv values than the sub-surface area. Minimum COD value was not less than 0.2 mm (0.008 in.) for as-welded metal and not less than 0.7 mm (0.03 in.) for stress-relieved weld metal at -60°C (-76°F)—Fig. 11B.

Although the COD value increased with the stress relief, the Cv absorption energy slightly decreased for reasons not yet clear.

The flux can also be applied to sea berths using multipass techniques.

LPG Tanks

An agglomerated $TiO_2-B_2O_3$ bearing flux was applied to weld walls of LPG

tanks. The plates were Al killed low temperature grade steel with a typical chemical composition of 0.072% C, 0.19% Si, 1.07% Mn, 0.014% P, 0.002% S and 0.24% Ni. The plates were prepared with single V-groove welds and welded in a horizontal position with heat input of about 20 kJ/cm (51 kJ/in.). The groove of the final side was prepared by arc gouging before welding.

Cv, tension and COD tests and chemical analysis of weld metals were carried out. The side-notched Cv test bars and tension test pieces were cut from the backing side of the weld metals. Full thickness COD test specimens were cut according to British Standard 5162:1979.

An example of the chemical composition of weld metals was 0.07% C, 0.12% Si, 1.37% Mn, 0.014% P, 0.004% S, 0.07% Ni, 0.027% Ti, 0.003% B and 0.036% O. Tensile strength was 609 MPa (88 ksi) and average Cv absorption energy was 193 J at -50°C (-58°F); COD values at -50°C (58°F) were not less than 2.7 mm (0.106 mm).

Ships

The other sector of application for $TiO_2-B_2O_3$ bearing fluxes is in ship building. Single pass submerged arc welding with flux-copper backing was used to join 50 kg/mm² (71 ksi) class ship steel (32 mm or 1¼ in. thick) at a heat input of 197 kJ/cm (500 kJ/in.). The tensile

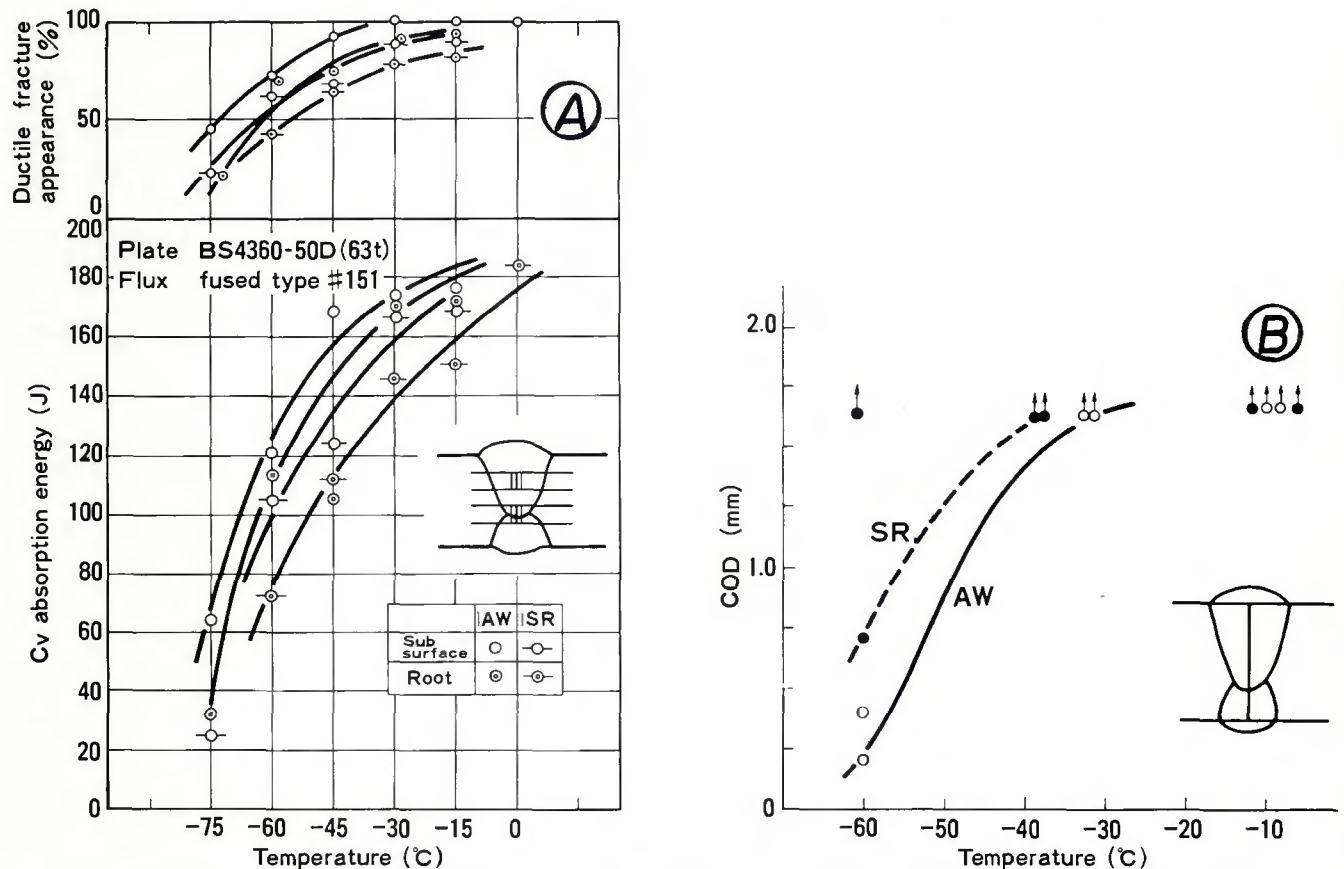


Fig. 12—Toughness of weld metal when $TiO_2-B_2O_3$ bearing flux applied to BS4360-50D class thick plate. A—Cv toughness; B—COD value

strength of welded metals was about 540 MPa (78 ksi), and the Cv absorption energy of the weld metal was about 100 J at -10°C, i.e., 14°F (Ref. 10).

Line Pipes

Flux of this family is applied to weld seams of API-5LX-70 class arctic-use line-pipes using single-pass techniques on each side of the weld.

Conclusion

The object of the research discussed in this paper was to develop fluxes which can consistently microalloy weld metal with Ti and B. The most probable way seemed to be the addition of Ti and B to the weld metal by reducing their oxides (TiO₂ and B₂O₃) in fluxes during welding. After discovering the design principle of TiO₂-B₂O₃ bearing fluxes, new fluxes with the following characteristics were successfully developed and applied:

1. Weld metals deposited using these fluxes contain less oxygen than those using other marketed fluxes at the same basicity index, because the stable oxides of TiO₂ are used as a main component instead of SiO₂.
2. The fluxes can consistently microalloy weld metals with optimum amounts of Ti and B over a wide range of heat inputs.
3. The fluxes have good arc stability so that the N content in weld metal can be reduced.
4. The slags of these fluxes easily detach themselves from weld beads even at a root pass of multipass welding because of successful elimination of the formation of perovskite (TiO₂CaO).
5. The optimum amount of Ti content in weld metal ranges from 0.015 to 0.025%, and for B content it is the equivalent molar weight of N in weld metals.
6. The FATT lowers with decreasing N content.

When optimum amounts of Ti and B are added to weld metals, the weld metals have following the characteristics:

1. High Cv absorption energy with appropriate tensile strength of weld metal.
2. Only slight deterioration of FATT in as-welded metal with the addition of Nb.

When new flux was applied to weld BS4360-50D class steel and to Al killed low temperature steel, as-welded metals showed a good minimum COD value

even at low temperature; this is usually difficult to obtain with commonly marketed fluxes.

References

1. Suzuki, H.; Sekino, S.; Mori, N.; Tanigaki, H.; and Sugioka, I. *Development of CaF₂-Ti-B type submerged-arc tubular wire with high notch toughness.* IIW Doc. II-583-71, IX-750-72.
2. Garland, J. G., and Kirkwood, P. R. 1975. Towards improved submerged arc weld metal, part 2. *Metal Construction and British Welding Journal* 7(6):720.
3. Wanke, R. 1973. Lineare thermischer ausdehnungs koefizient von schweisspulverschaken und berechnung ausden ausdehnungswerten. *Schweissen und Schneiden* 25 H7: S252-254.
4. Reser, M. K. ed. 1974. *Phase diagrams for ceramists*, 3rd ed. American Ceramic Society.
5. Buessen, W. R.; Thielke, N. R.; and Sarakavskas, R. V. 1952. Thermal expansion hysteresis of aluminum titanate. *Ceramic Age* 60(10):38-40.
6. Nagano, K.; Takami, T.; and Koyama, K. 1980. On the behaviour of partition reaction of Ti and B in SAW. *Preprint of JWS Spring Conference: 78-79* (in Japanese)
7. Kubaschewski, O.; Evans, E. II.; and Alcock, C. B. A. 1967. *Metallurgical thermochemistry*, 4th ed.
8. Caughlin J. P. 1954. *Contributions to the data on theoretical metallurgy: XII heat and free energy of formation of inorganic oxides.* Bulletin 542. Bureau of Mines.
9. Elliott, J. F. and Cleiser, M. 1960. *Thermochemistry for steel making*. Vol. II. Addison-Wesley Publication Co.
10. Horigome, T.; Kanazawa, S.; Tsunetomi, E.; Mimura, H.; Nakashima, A.; Shinmyo, K.; and Okamoto, K. 1967. Newly developed 50kg/mm² ship steel and its welding material. *Proceedings of welding of HSLA [microalloyed] structural steels: 679-705, 786-788.* Metals Park, Ohio: American Society for Metals.
11. Horigome, T.; Tsunetomi, E.; Shinmyo, K.; Nagano, K.; Mori, N.; and Kato, T. 1978. Study of Ti-B type welding material for high heat input submerged arc welding of 50kg/mm² class steel. *Jnl Jpn Welding Soc.* 47:18-25 (in Japanese).
12. Mori, N.; Homma, H.; Okita, S.; and Wakabayashi, M. 1981. Mechanism of notch toughness improvement in weld metals containing Ti and B. *Jnl Jpn Welding Soc.* 50 #2:35-42 (in Japanese).
13. Mori, N.; Homma, H.; Wakabayashi, M.; and Okita, S. *Ti-B kei yosetsu kinzoku no zaishitsu tokusei.* *Jnl Jpn Welding Soc.* 50 #8:74-81 (in Japanese).
14. Homma, H.; Mori, N.; Saito, S.; and Shinmyo, K. *Effects of titanium-boron and niobium additions on the mechanical properties of submerged arc weld metals.* IIW Doc. IX-1072-78; Doc XII-E-10-78.

Appendix: The Effect on Composition of Weld Metals of the Reduction Ratio of Oxide in Flux and the Dilution of a Base Metal Plate.

For simplicity of calculation, a direct pile up weld bead is assumed, namely, the n-th pass formed with α part of (n-1)th weld metal and (1-α) part of the electrodes. It is also assumed that neither the base metal plate nor the electrode contain a considered element.

Where the apparent partition coefficient (L) is a ratio of the element content in the slag (Cs) to the element in the weld metal (C_M), the mass conservation rule requires:

$$\alpha C_M^{n-1} W_M + C_F W_S = C_M^n W_M + C_S W_S \tag{1}$$

where C_Mⁿ = the element content in n-th pass weld metal; C_F = the element content in the flux; W_M = weight of fused weld metal to n-th pass weld metal; W_S = weight of fused slag;

One can assume C_M^{base plate} = 0 so that by solving the recurrence equation (1), the element content of n-th pass weld is given as:

$$C_M^n = \frac{C_F Y}{(1 + Y^* L - \alpha)} [1 - (\alpha / (1 + Y^* L))^n] \tag{2}$$

where Y is the fused weight ratio of the fused slag to the fused weld metal.

Since α/(1 + Y*L) is usually less than 1, when n goes to infinity, C_Mⁿ converges to the coefficient before the square bracket in right hand side of equation (2). Therefore, one can define the condensing factor as:

$$C^{infty} / C^1 = (1 + Y^* L) / (1 + Y^* L - \alpha) \tag{3}$$

One can see from equations (2) and (3) that the changing of element content with pass number is practically negligible when the element is added by reducing its oxide in the flux and when the apparent partition coefficient is large enough.

On the other hand, when Ni in the base metal plate and Mo in the electrode are considered, one has to replace equation (1) with:

$$C_W^n = \alpha C_W^{n-1} + (1-\alpha) C_W^E \tag{4}$$

where C_Wⁿ = the element content in the n-th pass weld metal, and C_W^E = the element content in the electrode.

For Ni and Mo in this paper, equation (4) can be rewritten as:

$$C_{Ni}^n = \alpha^n C_{Ni}^{base plate} \\ C_{Mo}^n = (1-\alpha^n) C_{Mo}^E \tag{5}$$

Therefore, one can see from equation (5) that Ni in the weld metal decreases and Mo increases with an increasing weld pass number.