Communication

Tuning Weld Metal Mechanical Responses *via* Welding Flux Optimization of TiO_2 Content: Application into EH36 Shipbuilding Steel

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A series of TiO_2-containing basic-fluoride-type agglomerated fluxes was applied to join EH36 shipbuilding steel under high heat input SAW. The effects of TiO_2 content on composition, microstructure features, inclusions characteristics, and mechanical properties of ensuing weld metals (WMs) were systematically investigated. 6 wt pct TiO_2 leads to the most optimal mechanical properties. Such behaviors were elucidated *via* transfer of alloying elements, which enables a good combination of acicular ferrites (AFs) and accompanying microstructures.

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Submerged arc welding (SAW) joins metals by heating them in the arc established between the wire electrode and the base metal (BM) with the arc shielded under molten slag and flux. Due to high deposition rate, SAW is widely applied in fields of heavy industrial applications, such as pressure vessels, shipbuilding, pipelines, and offshore structures. Submerged arc-welded joint consists of three parts: BM, heat-affected zone, and weld metal (WM). As WM is a production of physical and chemical reactions of the molten weld pool and flux, it is essential to develop flux to achieve satisfactory reliability.[1,2] As for the flux, in addition to the physical requirements (melting temperature, viscosity, density, detachability) it must satisfy, the chemical composition of flux is important as it pertains to the final composition, microstructure, and mechanical properties of WM.[3,4]

Tremendous effort was exercised to investigate the correlation of flux composition and the ensuing WM microstructure, which, in turn, dictates the final mechanical responses. For instance, Dallam *et al.*[1] studied the effect of CaF_2-CaO-SiO_2-based fused fluxes on a Nb-microalloyed high-strength low-alloy steel and found that O content, which attained its optimum value ranging from 200 to 300 ppm, was one of the most important factors governing the WM mechanical properties. Kohno *et al.*[5] developed $TiO_2 + B_2O_3$-bearing fluxes, which could transfer Ti and B to WM, and revealed that optimal mechanical properties were obtained when Ti and B in WM reached 0.02 and 0.0045 wt pct, respectively. Roy *et al.*,[6] on the other hand, offered detailed investigations of the influence of TiO_2 addition into the flux on the bead geometry and grain size of WMs and concluded that 5 wt pct TiO_2 led to the best bead geometry and grain size reduction with higher TiO_2 addition.

In recent years, to achieve higher welding efficiency, multielectrode SAW with higher heat input has been widely applied. However, when high heat input is exerted, significant austenite grain coarsening may occur and certain brittle microstructures, including upper bainite, ferrite side plate, and grain boundary ferrite, which provide convenient crack propagation paths, tend to form.[7,8] One of the major countermeasures is to develop suitable welding fluxes accommodating high heat input by introducing acicular ferrite (AF) promoting components, such as TiO_2, ZrO_2, or even rare earth oxides, through the adjustment of flux composition and subsequent alteration of WMs.[6,9–12] As such, AFs, inherently interwoven microstructure in nature, bode well for crack propagation prevention, leaving sufficient space for toughness enhancement, even if under high heat input.

In this study, TiO_2-containing basic-fluoride-type fluxes were tested to enhance mechanical properties of welded EH36 shipbuilding steel subjected to high heat input SAW. A commercial CaF_2-SiO_2-MgO-Al_2O_3-based agglomerated flux is selected as the base for its capability to offer low-temperature toughness and high heat input detachability.[3] The effects of TiO_2 content were fully investigated with regard to major elemental transfer behaviors, inclusion distribution characteristics, salient microstructure features, as well as resultant mechanical properties of the WMs.

Four fluxes containing 1, 6, 11, and 16 wt pct TiO_2 were prepared by mechanical mixing of commercial CaF_2-SiO_2-MgO-Al_2O_3 base agglomerated fluxes (Atlantic, China) with reagent-grade titanium oxide in a V blender (Delixi) at 0.5 Hz for 1 hour. Chemical compositions of the fluxes were determined by X-ray fluorescence (S4 Explorer), as shown in Table I. Multipass (800 A/32 V, DC + 650 A /36 V, AC) SAW (double-wire, Lincoln Electric Power Wave AC/DC 1000 SD (Lincoln Electric, China)) was performed with a 50 deg single-V groove on the BM of EH36 shipbuilding steel. The welding speed was set as 50 cm/min

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and the total heat input of 58.8 kJ/cm was used. The compositions of the BM, electrode, and four distinctive WMs are summarized in Table II.

WMs were cross sectioned and polished by standard procedures. Microstructures of all samples were etched by nital solution (4 wt pct) and observed by a field emission–scanning electron microscope (FE-SEM, model: Hitachi SU8010). The volume percentage of AF was determined by means of the linear intercept method with five fields being taken at a magnification of 500 times. The morphology, composition, size, and number of inclusions were analyzed by SEM (acceleration voltage: 10 kV) with an energy-dispersive spectrometer (EDS). The number density of inclusions was calculated under 3000 times magnification in the area of 0.19 mm × 0.14 mm, and only inclusions whose composition was confirmed by EDS analysis were taken into account. Tensile tests were conducted at room temperature using three specimens with a gage diameter of 12.5 mm and gage length of 50 mm according to ASTM E-8.[13] Charpy impact tests were performed at − 40 °C to assess notch toughness, for which three specimens (55 mm × 10 mm × 10 mm) were taken from the fusion zones of the WMs.

Figure 1 presents plots of Charpy impact energy and tensile strength values as a function of TiO_2 content in the welding flux. It can be seen that both Charpy impact energy and tensile strength increase from 50 to 81 J and 708 to 726 MPa, when the TiO_2 varies from 1 to 6 wt pct, respectively. However, such a concurrent rising trend terminates when further TiO_2, 11 and 16 wt pct, is added into the flux. In other words, both values reach their maxima when TiO_2 is at 6 wt pct. This is rather remarkable and different from previous work conducted by Paniagua-Mercado *et al.*,[9] in which Charpy impact energy was found to be continuously improved with higher TiO_2 content in fluxes.

To further illustrate the mechanism of mechanical properties enhancement by TiO_2 addition into fluxes, the relationship between TiO_2 content and the AF volume fraction of the WMs has been summarized and is plotted in Figure 2. It is observed that the maximum AF volume of 41 pct occurs when 6 wt pct TiO_2 is contained in flux. Such a phenomenon is similar to the changing trends for Charpy impact energy and tensile strength variations, which implies that the AFs provide a definitive role in exhibiting a good combination of strength and toughness for WMs due to AFs' fine interlocking structure and their small effective packet sizes.[14] The inset SEM micrograph shows a typical scenario on how inclusions are intertwined with AFs. The fact that impact energy increases with higher AF volume fractions,[9,15,16] even under huge heat input,[8] has been extensively discussed and is consistent with the results of the present work, although the mechanism of AFs' formation is not fully understood.

It is well established that certain types of inclusions, when in appropriate morphology, compositions, and sizes, are more inducing for the nucleation of AFs.[15,17,18] In this regard, statistical number density mapping, together with the most representative inclusions encountered in this study, has been generated and is presented in Figure 3. Typical inclusions dispersed in WMs are mainly Ti-Al-Mn-S-O-(Mg)-type oxides, and their shapes are nearly spherical. A salient feature on inclusion size is that most of the inclusions, for any flux-treated sample, are predominantly small in nature, ranging from 0.3 to less than 2 μm. In addition, it is clearly seen that TiO_2 content has a significant impact upon inclusion number density values, which is postulated to be largely associated with varied O and Ti contents in the WM.[9,19,20] Another outstanding feature is the presence of the highest value, up to 280/mm^2, for the 6 wt pct TiO_2 sample, which is a several-fold spike as compared to other compositions. Kim *et al.*[8] performed SAW of high heat input and found that the volume fraction of AF was in proportion to the number density of inclusions whose sizes were smaller than 2 μm. Also, it is reported that larger inclusions are preferable sites for nucleation of AF, but with a further increase of

Table I. Chemical Compositions of Target Fluxes (Weight Percent)

Fluxes	CaF_2	Al_2O_3	MgO	SiO_2	MnO	CaO	TiO_2	K_2O	Na_2O	FeO	ZrO_2
1	38.34	19.71	16.97	16.32	2.89	0.98	1.02	0.58	1.84	1.32	0.03
2	35.12	18.67	16.55	16.25	2.62	1.25	5.88	0.60	1.67	1.35	0.04
3	32.75	17.59	15.79	15.78	2.50	1.08	10.77	0.56	1.87	1.26	0.05
4	29.94	16.88	14.98	14.99	2.37	1.03	15.87	0.78	1.84	1.29	0.03

Table II. Chemical Compositions of the BM, Electrode, and WMs (Weight Percent)

	C	O	Mn	Si	Ti	Al	Ni	Mo	Cr
EH36	0.035	0.0003	1.42	0.16	0.015	—	0.12	0.62	0.02
Electrode	0.105	0.0003	1.8	0.18	—	—	—	—	—
WM-1	0.062	0.033	1.73	0.35	0.016	0.014	0.643	0.474	0.061
WM-2	0.068	0.039	1.82	0.383	0.023	0.015	0.718	0.531	0.063
WM-3	0.057	0.043	1.5	0.376	0.022	0.013	0.683	0.486	0.058
WM-4	0.06	0.049	1.43	0.347	0.021	0.012	0.706	0.501	0.058

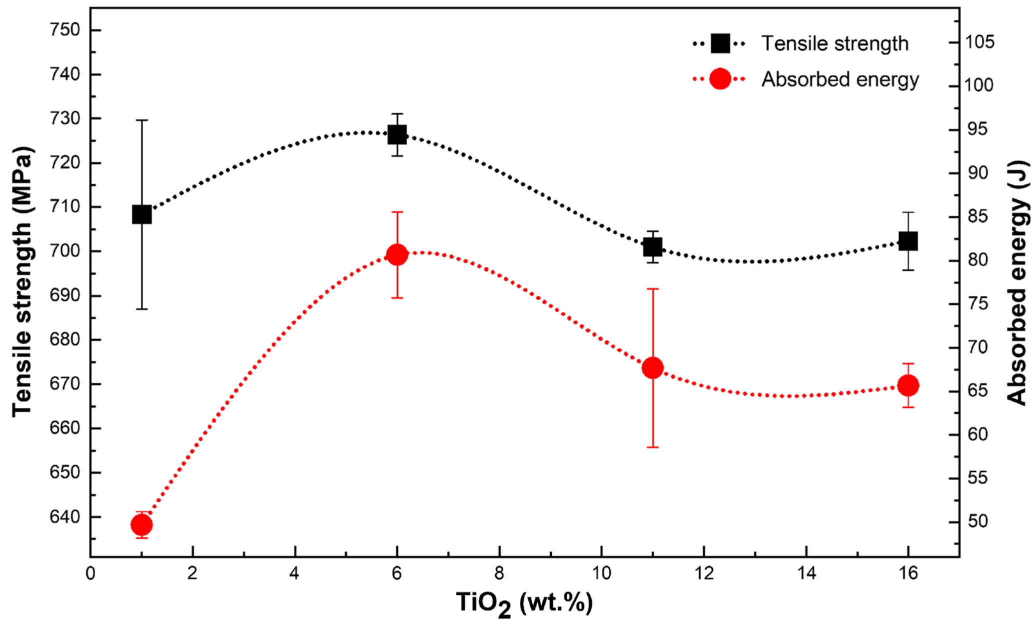

Fig. 1—Variation of Charpy impact energy and tensile strength as a function of TiO_2 content in the welding flux.

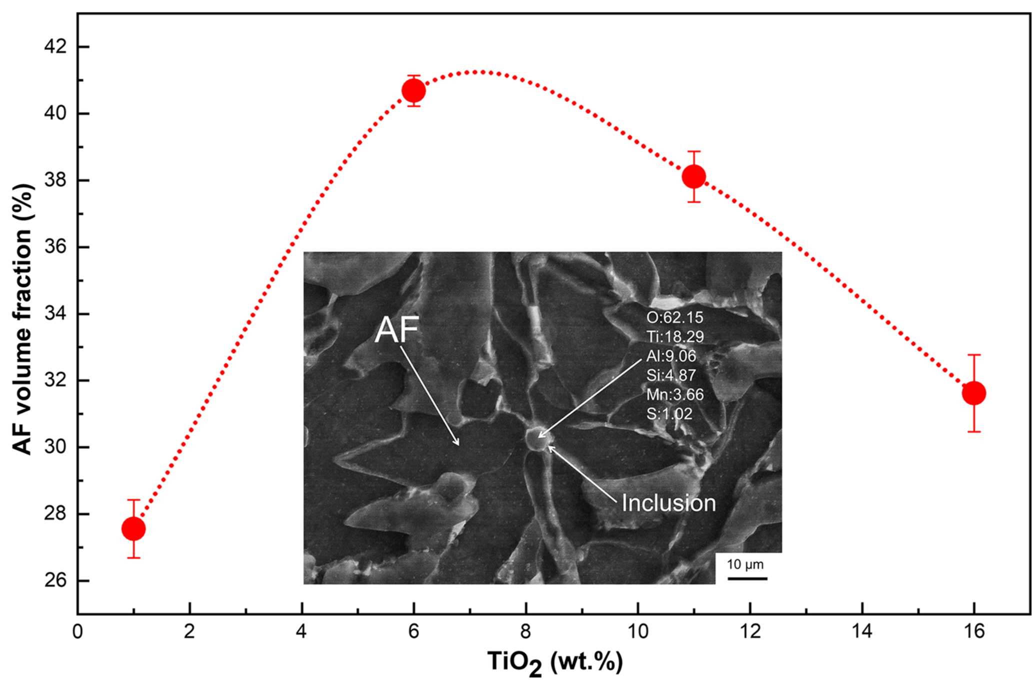

Fig. 2—Variation of AF volume fraction as a function of TiO_2 content in the welding flux. The inset figure presents a representative SEM micrograph demonstrating AFs being nucleated around inclusions when TiO_2 is 6 wt pct.

inclusion size, the probability of AF nucleation remains constant.[21] In the present work, the number densities of inclusions in 1, 6, 11, and 16 wt pct are 4403, 15,725, 10,175, 6068 N/mm^2 and their average sizes are 607, 792, 682, and 665 nm, respectively.

As shown in Table II, compositions of WMs are significantly altered through the addition of different TiO_2 into fluxes due to the slag-metal reactions that occurred during SAW.[22,23] It should be pointed out that the transfer of major elements, such as Ti and O, dictates the final microstructures.[1,14,24] In this regard, an alternative plot showing O and Ti content variation is constructed in Figure 4.

It can be seen from Figure 4 that the increase in TiO_2 from 1 to 16 wt pct is accompanied by an increase in O level from 330 to 490 ppm in the WMs. It is well established that O less than 200 ppm results in a lack of nucleation sites for AFs, whereas too much O, higher than 500 ppm, leads to a high proportion of polygonal ferrite.[8,17] The O levels of WM-1 to WM-4 are found in the optimal range; therefore, higher AF fractions are anticipated.

It is accepted that TiO_2 in fluxes is susceptible to decomposition under the influence of high-temperature welding plasma.[25] In the droplet reaction zone, decomposition of TiO_2 (into suboxides and oxygen) occurs and the O level of the droplet is significantly improved. In the weld pool, the slag-metal reaction will take place

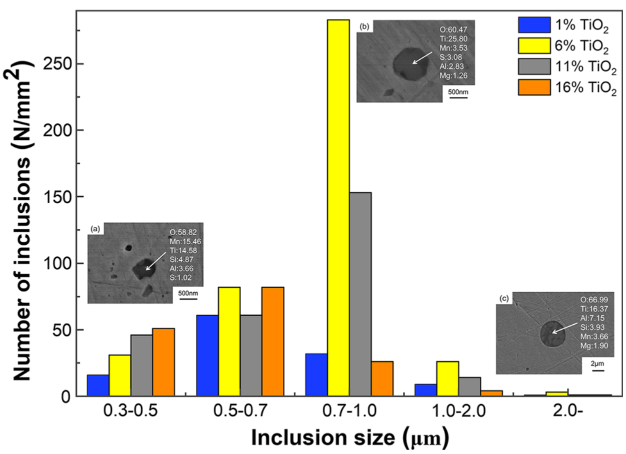

Fig. 3—Inclusion size distributions for WMs treated by different fluxes. The inset figures are typical inclusions found in (*a*) 0.3 to 0.5 μm, (b) 0.7 to 1.0 μm, and (*c*) > 2-μm ranges.

according to Eq. [1], which enhances the O content of WMs and promotes the transfer Ti to the WMs.[23]

$$(TiO_2) = [Ti] + 2[O] \quad [1]$$

The reaction products float up into the molten slag or remain as nonmetallic inclusions in the WMs. Moreover, the Ti-containing nonmetallic inclusions remaining in the WM promote the formation of AF. When the TiO_2 content is higher than 6 wt pct, the transfer of Ti is likely suppressed, as shown in Figure 4. This phenomenon could be explained in terms of the slag-metal reaction, which is highly influenced by the O potential of flux as a higher O level in the WM may lead to the increased consumption of Ti.[22,23] The maximum of Ti content in WM is obtained in 6 wt pct TiO_2-containing flux, as illustrated in Figure 4. It is interesting to note that the inclusion densities and average sizes do not increase with higher O in WMs, as observed in Figure 3. It seems that Ti content probably constitutes the main factor governing inclusion density, which is consistent with the results of previous work.[9] Further investigations on inclusion float-out characteristics, solidification behavior, and thermal cycle effects are being conducted. It should be noted that the observation in this work might have been influenced by some unintended increase of other flux components, except for TiO_2.

EH36 shipbuilding steel was processed under 58.8 kJ/cm heat input by CaF_2-SiO_2-MgO-Al_2O_3 agglomerated fluxes with varied TiO_2 content. It is found that TiO_2 content exerts remarkable impact over inclusion distribution characteristics, microstructure features, and

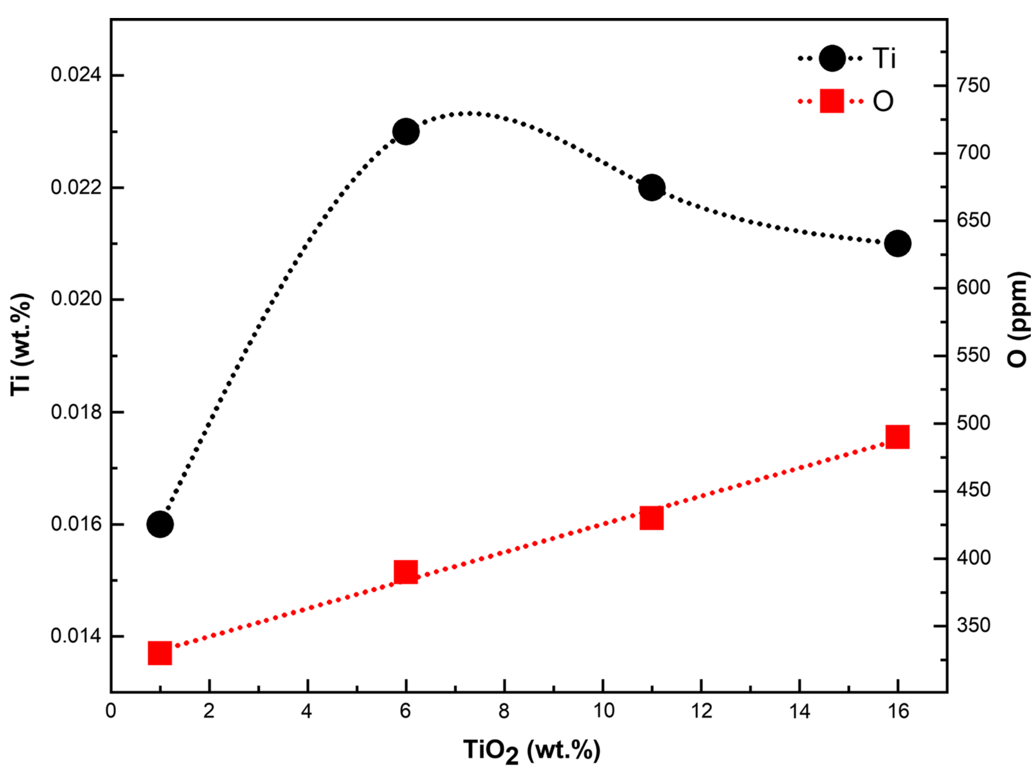

Fig. 4—Variations of O and Ti composition in WMs.

mechanical behaviors. A best combination of mechanical properties, including Charpy impact energy and tensile strength, is found when TiO_2 is at 6 wt pct, which is accompanied by the highest achievable Ti content and maximum fraction of AF in the WM. It is postulated that TiO_2 in fluxes is susceptible to decomposition and the subsequent reaction would significantly improve the O of WMs and promote the transfer Ti to WMs.

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