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Structure of Slag (XI)†

-Role of TiO₂ in Slag-

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Abstract

In this review, the role of TiO_2 in flux is summerized from the viewpoints from the effect of Ti contained in weld metal and the problem on detachability of slag crust from the weld bead.

KEY WORDS: (TiO₂) (Weldability) (Slag) (Basicity of Slag) (Chemical Reaction)

1. Introduction

As previously discussed¹⁾, TiO₂ as amphoteric component in slag shows characteristic behaviors on basicity, physical properties and detachability of slag crust from weld bead. In some reports,²⁾⁻³⁾ the beneficial effect of TiO₂ addition in flux is described. However, it yet remains unclear whether TiO₂ addition in flux has decisive effect on the weldability. In this review, it is summerized how TiO₂ addition in flux gives influences on welding conditions such as the transfer of metal droplet, detachability of slag crust from weld bead, chemical reaction concerning metallic and gases contents in weld bead, and mechanical properties. Continuously, the structural analysis using physical means is summerized to determine the configurational behavior of Ti ion in the molten slag.

2. Fundamentals

2.1 Effect of TiO₂ on the basicity of slag

If we are forced to say, it has been thought that ${\rm TiO}_2$ in slag could act as weak acidic component. To define slag basicity, the following description has been given.

a) Mori designation:
$$B_L = \Sigma \ a_i \ N_i = a_1 \ N_1 + a_2 \ N_2 + \cdots$$

where, a_i ; SiO_2 (-6.31), TiO_2 (-4.97), Al_2O_3 (-0.2), (1)

b)
$$B_{I}$$
 = [CaO + MgO + SrO + Na₂O + K₂O + Li₂O + 1/2 (MnO + FeO)]/[SiO₂ + 1/2(Al₂O₃ + TiO₂ + ZrO₂)]⁶⁾⁻⁷⁾ (2)

c) B =
$$CaO + MgO + FeO + MnO + K_2O + Na_2O/SiO_2 + 0.78TiO_2^{8}$$
 (3)

2.2 Effect of TiO₂ on slag-metal reaction

2.2.1 Sulfide capacity

In recent years TiO2 has been indentified as potential substitute for CaF₂ as the flux for steelmaking slags.⁹⁾ When compared the difference of sulfide capacity in the system, CaO-TiO2-MgO and CaO-SiO2-MgO, the former showed better desulfurizing activity. 10 In Figure 1, the effect of TiO2 on sulfide capacity of CaO-TiO2-SiO2 melts at 1500°C is shown. From this result, it can be seen that at a constant lime concentration the substitution of TiO₂ for SiO₂ raises the sulfide capacity. According to another discussion; 11), the formation of TiO₆⁸⁻ could be considered in the system SiO₂-TiO₂ but Ti⁴⁺ ion occupies the tetrahedral position in silicate network at the higher ratio of $\mathrm{SiO_2/TiO_2}$. At that time, Ti^{4+} ion does not take symmetrical configuration and therefore can distort easily. For that reason, it can be considered as more basic composition than theoretically thinking.

As given in Table 1, sulfur-partition ratio is increased with increasing TiO₂ content in the blast-furnace type slag. This behavior cannot explain from the data given by Duffy et al.¹²⁾ In Table 2, optical basicity of oxides is given.

The basicity moderating parameter:

$$\gamma = 1.36 (x - 0.26) \tag{4}$$

where x is electronegativity of cation

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Optical basicity: $\Lambda = 1/\gamma$ (5)

For a given slag: $\Lambda = X_A \Lambda_A + X_B \Lambda_B$, (6) where X_A and X_B are the equivalent cation fractions of A and B

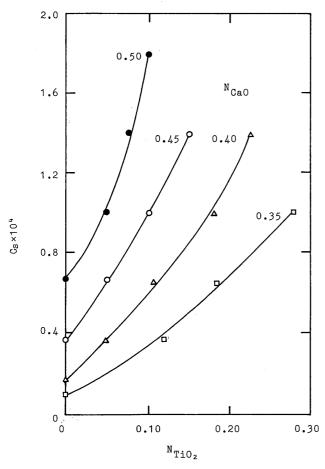


Fig. 1 The effect of TiO_2 on sulfide capacity of CaO- TiO_2 - SiO_2 melts at $1500^{\circ}C^{10}$)

2.2.2 Activity of MnO in the system MnO-SiO₂-TiO₂

In Figure 2, contours of iso-activity of MnO in the system $MnO-SiO_2-TiO_2$ are shown.⁹⁾ For a given mole fraction of MnO, the replacement of SiO_2 by TiO_2 increases a_{MnO} . From this result, it will be considered that TiO_2 behaves less acidic than SiO_2 . This fact is an important problem to determine the reduction behavior of manganese from MnO in slag.

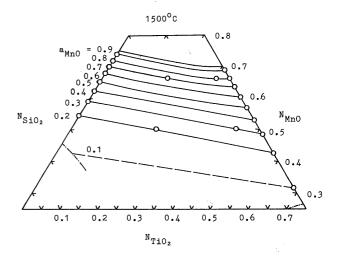


Fig. 2 The contours of iso-activity of MnO in the system MnO-SiO₂-TiO₂⁹⁾

2.2.3 Gas shield Arc process

The introduction of titanium into the weld during gasshielded consumable electrode welding was carried out by means of the filler metal and the parent metal.¹³⁾ As conclusion, it was determined that the transfer coefficient of titanium added to the weld metal through the electrode and the parent metal was similar. The oxidation of titanium decreases with a reduction in the welding current

Table 1 Effect of TiO₂ addition on sulfur partition between slag and metal¹²)

Composition (wt%)				C ×105	(%,5)/[%,5]	0/ C ₀ O /(0/S;O ±0/A1 O)	
CaO	SiO ₂	Al_2O_3	TiO ₂	C _s x10	[%3]/[%3]	%CaO/(%SiO ₂ +%Al ₂ O ₃)	
39.8	49.2	11.0	0.0	3.7	15.0	0.66	
38.6	47.1	10.1	4.2	4.2	17.0	0.67	
37.5	45.3	9.0	8.2	4.6	18.6	0.69	
36.4	43.5	7.9	12.2	5.0	20.0	0.71	

Table 2 Optical basicity of oxides¹²⁾

Oxide	CaO	MgO	Al_2O_3	TiO ₂	SiO ₂
Λ	1.00	0.78	0.605	0.55	0.48

at the constant melting rate of the metal, and with an increase in the welding speed. The reason can be clarified with the difference of pool surface.

2.2.4 Covered electrode

It is widely known that in the development of new welding consumables the introduction of thermally stable oxides of titanium and aluminium in the compositions of fluxes and electrode coverings was found effectively instead of the relatively unstable oxides of manganese and silicon. (14),15) As shown in Figure 3, the concentrations

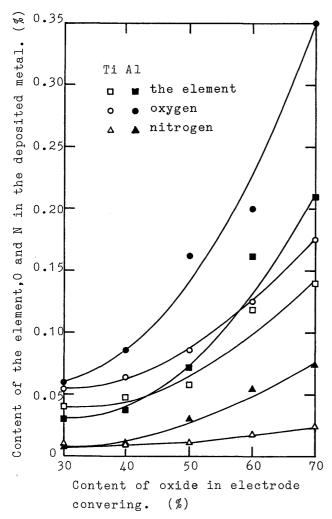


Fig. 3 The oxygen, nitrogen and titanium concentrations in deposited metal¹⁶)

of oxygen, nitrogen and titanium in the depesited metal could be confirmed.¹⁵⁾ The following chemical reactions were certified.

$$2/3(Al_2O_3) + 2[Si] \Rightarrow 2(SiO) + 4/3[Al]$$
 (7)

$$(TiO2) + 2[Si] \rightleftharpoons 2(SiO) + [Ti]$$
 (8)

$$2(SiO) = (SiO2) + [Si]$$
 (9)

It has been shown that reduction of Ti from slag was

the interaction of the oxide with silicon at the boundary of the heterogeneous system metal/slag in the reaction zone of welding. Further endogenetic oxide inclusion can be formed in the weld bead and the increase of oxygen content can be induced because of the difficult flotation. It is necessary to control the content of TiO_2 or $\mathrm{Al}_2\mathrm{O}_3$ in flux with extreme caution.

In general, the following chemical reactions should be considered to explain the increase of oxygen content in weld bead.

$$[Mn] + (FeO) \rightleftharpoons (MnO) + [Fe]$$
 (10)

$$2[Fe] + (SiO2) \Rightarrow 2(FeO) + [Si]$$
 (11)

$$2[Mn] + (SiO2) \Rightarrow 2(MnO) + [Si]$$
 (12)

However the reason why the oxygen content in weld bead abruptly decreases with the increament of slag basicity in the use of rutile type electrode not containing wustite is reduced to the suppression of SiO₂ reduction.

In the use of ilmenite electrode, the decrease of oxygen content in weld bead with the increase of the basicity value till $0.8 \sim 1.0$ can be recognized, but subsequent increase of the basicity value showed the increase of oxygen content in weld bead. The cause is analogized from the increase of activity of wustite in slag.

2.2.5 Submerged arc welding

Fused flux of the system $20 \text{SiO}_2 \cdot 15 \text{MnO-8CaO-} 57 \text{CaF}_2$ was used in SAW. In this case, reduction of MnO in slag occurred and therefrom the oxidation of chromium in wire was found. When TiO_2 was contained in flux, compound $\text{TiO}_2\text{-MnO}$ was formed in slag and the reduction of MnO in slag was suppressed due to the decrease of a_{MnO} . However the following reactions should be considered.

$$4\text{TiO}_2 \rightleftharpoons 2\text{Ti}_2\text{O}_3 + \text{O}_2 \tag{13}$$

$$2\text{TiO}_2 \rightleftharpoons 2\text{TiO} + \text{O}_2 \tag{14}$$

Another probable reason for the reduction in the manganese content of metal is attributed to the oxygen release due to ${\rm TiO_2}$ dissociation. The appropriate choice of ${\rm TiO_2}$ content behaves the suppression of MnO reduction in flux as well as oxidation of metallic silicon and manganese in wire. The increase of oxygen content in weld bead can be governed by the reduction of ${\rm SiO_2}$, MnO and ${\rm TiO_2}$ in flux.¹⁶⁾

When flux of the system CaF_2 -TiO₂-MgO in SAW was used, TiO₂ has the following disadvantages in comparison with $Al_2 O_3$.¹⁷⁾

- (1) It introduces the low viscosities of titanium slags in the molten state, and their high capacity for crystallization, and it means that these fluxes cannot have good technological properties from the standpoint of weld bead formation.
- (2) As the TiO₂ content of flux is increased, the depth of the weld also increases, and its width decreases.
- (3) As the amount of TiO₂ in the flux is increased, together with the initial concentration of silicon in the electrode wire, the amount of titanium in the deposited metal and also the oxide inclusion content increase.

When SiO_2 is present in substantial amounts in SAW flux, loss of alloying elements in filler metal due to oxidation by SiO_2 dissociation and appreciable amounts of silicon can be transferred to the deposited metal. For that reason, new low- SiO_2 flux was developed. With the use of system $SiO_2(3)$ - $[TiO_2 + MnO](60)$, the best properties such as as weldability and slag removal under the d-c condition was obtained.¹⁸)

In general, oxygen content and amounts of non-metallic inclusion in SAW weld becomes higher. As shown in Figure 4, the addition of ${\rm TiO}_2$ to standard flux gives good result on notched bar properties, especially at subzero temperature. It was believed that the reason was due to changes in weld microstructure. ¹⁹

As carbonate flux, the addition of Li₂CO₃ containing high proportion of CO₂ and the substitution of TiO₂ with

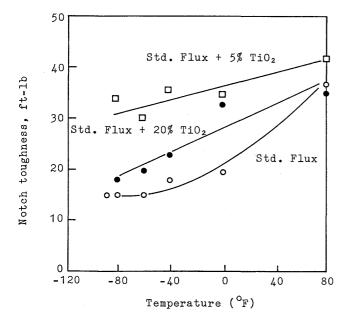


Fig. 4 Effects of TiO₂ addition to standard flux on notched bar properties of SAW weld metals¹⁹)

ZrO₂ has improved high fluidity because of jagged surface appearance of weld bead was admired.²⁰⁾

To prevent oxygen and nitrogen contamination during arc welding, oxygen potential as a function of basicity for TiO_2 -CaO and Al_2O_3 -CaO based slags at $2000^{\circ}C$ was calculated as shown in Figure 5. With a significant reduction in the oxygen potential when SiO_2 was replaced

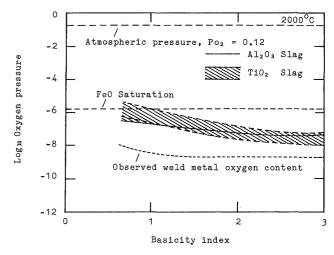


Fig. 5 Oxygen potential as a function of basicity of TiO₂-CaO and Al₂O₃-CaO based slags at 2000°C²¹)

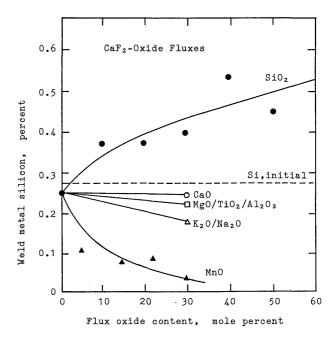


Fig. 6 Weld metal silicon analysis as a function of the percent metal oxide contained in the flux ²⁴)

with TiO₂ resulted the decrease of oxygen contamination in weld metal.²¹⁾

Because oxygen in weld metal causes a number of problems including porosity, loss of fracture toughness and reduced ductility, silicon and manganese contents was pursued with the addition of various components to CaF_2 . As shown in **Figures 6** and 7, the addition of TiO_2 produces a slight decrease of silicon content. On the other hand the increase of manganese content in weld metal occurs with the addition of TiO_2 .

Titanium reduction from the slag using ${\rm SiO}_2$ -free fused fluxes containing 10-30% ${\rm TiO}_2$ was studied. As shown in **Figure 8**, titanium content in weld metals as a function of the ${\rm TiO}_2$ and ${\rm FeO}$ activities of the slags coincided with the calculated value. ²³⁾

In Figure 9(a), the dependance of [Ti] and (TiO₂) is

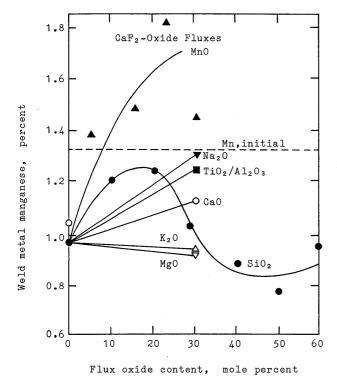


Fig. 7 Weld metal manganese analysis as a function of the percent metal oxide contained in the flux 22)

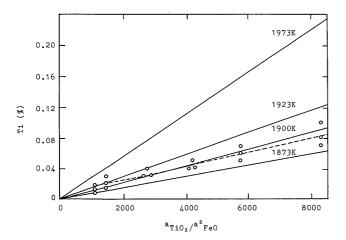


Fig. 8 The titanium content of weld metals as a function of the TiO₂ and FeO activities of the slags²³)

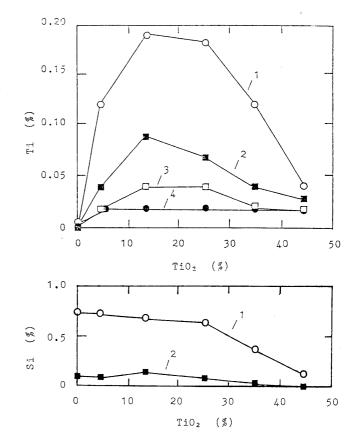


Fig. 9 The dependence of the content of titanium and silicon in the deposited metals on the TiO₂ content of flux²⁴) (1: Si/1.05%, 2: Cr/2.07%, 3: Mn/1.64%, 4: C/0.08%)

shown. From this result, it will be seen that the maximum reduction of TiO_2 in flux is in the range 13-25%. Although there exists possibility of silicon and carbon (or CO gas content) in metal to reduce TiO_2 in flux as recognized from the result of Figure 10, the significant role of silicon for reducing TiO_2 in flux was obtained from the result of Figure 9(b). The dependence of the hydrogen content in weld metal on the TiO_2 content in flux is shown in Figure 11. From this result, the significant effect of TiO_2 in welding can be understood.

On the contrary, as described later, the good impact toughness of weld metal was reported when flux containing TiO₂ was used. However, it is said that the metallurgical processes caused by the addition of TiO₂ to fluxes and the electrode coverings remains yet unsolved.²⁴⁾

In the system of $CaO\text{-}TiO_2\text{-}SiO_2$ flux modified with 5% CaF_2 , the most satisfactory SAW characteristics was found by using a flux composition of the system CaO(25)- $TiO_2(30)\text{-}SiO_2(40)$. Further it was noted that the welding performance was improved when a 1% manganese filler metal was used.²

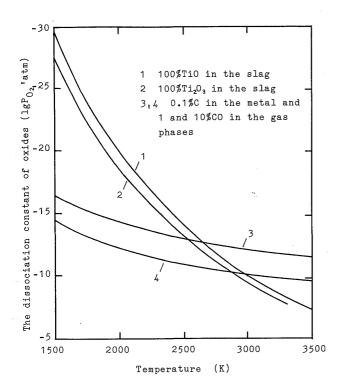


Fig. 10 The dissociation constant of oxides for: 1) 100% TiO in the slag, 2) 100% Ti₂O₃ in the slag, 3) 4) 0.1% C in the metal and 10% CO in the gas phases²⁴)

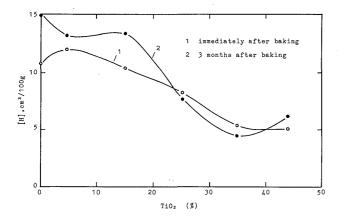


Fig. 11 The dependence of the hydrogen content of the weld metal on the TiO₂ content of the flux²⁴)

2.3 Effect of TiO₂ on cracking behavior

Weld metal manufactured by using rutile-coated electrode have insufficient resistance to hot cracking. With containing a large amount of iron powder into rutile-coated electrode, not only carbon content in weld metal but also the heterogeneous distribution of sulfur between around grain boundaries and within grains were reduced. From these effects, the resistance to hot cracking was modified.²⁵⁾

For good technological and metallurgical properties such as stable arc burning, satisfactory formation of weld metal with a smooth tradition to the base metal, a high resistance to pore formation, and efficient refining effect to reduce sulfur and phosphorus contents in weld metal, fused fluxes of the system, CaF₂-TiO₂-CaO-Al₂O₃ was developed. With the use of this flux, the primary structure having disoriented and equiaxial of welded joints was obtained.

And the mechanical properties were improved and the resistance to the formation of hot and cold weld metal cracks was also increased.²⁶⁾

2.4 Effect of TiO₂ on the transfer of metal droplet

Interrelation between marble content and the shape of metal droplet was investigated. Then the mutual ratio of marble and fluorspar (70:0, 60:10, 50:20, 40:30, vise versa) was changed with the fixed composition such as feldspar (10), TiO_2 (4), ferromanganese (8), ferrosilicon (7) and aluminum powder (1), and the following results were obtained:

- (1) The increase of marble contnet showed aerodynamical effect to be controlled the direction of gas stream and intensified. Accordingly it resulted molten droplet to be finer.
- (2) The increase of oxygen potential due to the increment of marble content reduced the decrease of interfacial tension between slag and metal, and at the same time assisted in braking droplet. Of course, the reduction of the concentration of silicon and manganese in weld metal is introduced.²⁷⁾

When CO_2 welding with cored wire based on the TiO_2 - Fe_2O_3 system flux was used, the manganese and silicon are mostly oxidised in the droplet stage. In the pool stage the rate of oxidation of manganese and silicon was very much lower.²⁸⁾

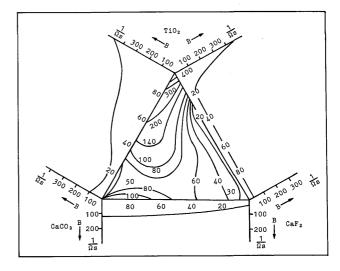


Fig. 12 Influences of CaCO₃, CaF₂ and TiO₂ on the arc stability (mole%)³⁰⁾

The emission of positive ions by welding slags containing about $20\% \, \text{TiO}_2$ and the effects on the stability of the a.c. was investigated. However it is necessary to know the individual effect of TiO_2 on the stability of the a.c. in future. ²⁹⁾

The effect of TiO₂ addition on the stability of the a.c. has been studied when basic electrode with the system CaCO₃-CaF₂-TiO₂ flux was used.

As shown in Figure 12, it became evident that the increase of TiO₂ strengthens the stability of arc. On the other hand, the addition of CaF₂ above 20% gave harmful effect on the stability with the following reaction.³⁾

$$2CaF_2 + TiO_2 = TiF_4 + 2CaO$$
 (15)

2.5 Effect of TiO₂ on physical property of molten slag

The effect of ${\rm TiO}_2$ addition on surface tension of molten slag was investigated. In Figure 13, the temperature dependence of the surface tension of basic coated electrode with and without ${\rm TiO}_2$ addition is shown.

From this result, it will be understood that small additions of TiO_2 makes it possible to decrease the surface tension with a slight "weakening" of its temperature dependence.³¹⁾

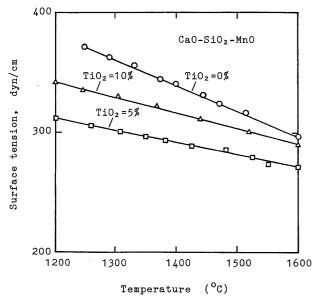


Fig. 13 The temperature dependence of the surface tension of basic coatings with the variation of TiO₂ content³²⁾

3. Interfacial Problems between Solidified Slag and Weld Metal

Because of the difficulty to know elemental distribution at the interface between solidified slag and weld metal, the application of mass spectrometry of secondary ion emission was done. In the case of basic flux cored electrode and steel alloyed with titanium, secondary ion sputtered from slag crust touched to weld metal showed high-intensity peaks of Ti⁺ and TiO⁺.

Likewise the slag crust which is difficult to detach from weld metal containing vanadium showed mainly secondary ion of VO. From these results, the interlayer found at the slag-metal interface in the welding of titanium and vanadium alloyed steels, which causes poor separation of the slag, consists mainly of the lower oxides of these elements.³²⁾

To know the surface texture of weld metal alloyed with titanium and vanadium, observation using SEM was performed. Two types of covered electrode as following were compared in combination with the slag removal.

- (1) Separation of slag crust was difficult in the combination of steels containing 2%Ti and 2.9%V with carbonate-fluoride type flux, which contains 20% marble, 23% fluoride, 15% aluminum powder, 38% iron powder, 3%FeMn and 0.7%FeSi.
- (2) Separation of slag crust was easier in the combination of low carbon steel with rutile-carbonate type flux.

It was determined that dislocation density in the case of (1) is greater than that of (2). It was concluded that the formation of strong bond between the slag and the metal is companied with structural changes in the surface layer of the deposited metal. The greater the non-correspondence (difference of lattice parameters of MeO formed in slag and weld metal) is, the greater the dislocation density in the surface layer of the deposited metal becomes. By that means, elastic stresses can be compensated²³⁾

Continuously the mechanism of the bond between the slag crust and the weld surface was studied. There are two factors to decide the difficulty of slag detachability from the weld bead. (1) Chemical reaction between the slag and the weld metal, and (2) locking of slag in defects such as undercutting and partial penetration in the weld bead. To know the cause, the components such as marble, magnesite, hematite, aluminium and iron powders in coated electrode were changed. The phase composition of the slag crust was analysed with X-ray diffraction. The results obtained are as follows:

- (1) To do easier the removal of the slag crust from the weld bead, intermediate layer having nearer lattice parameter to that of α -iron and therefore that is easier to grow epitaxially with the lattice of matrix, must not be formed at the interface.
- (2) The formation of spinel at the interface cannot be principal factor determining detachability. It must be considered the sort of spinel formed.
- (3) TiO riched at the interface between slag and weld bead has harmful effect on detachability. For that

reason, change to TiO₂ by oxygen potential control is necessary.³⁴⁾

Using mathematical formulation and the simple experiment, it was verified that the transfer of titanium element in steel to interfacial oxide layer depends on square root law.³⁵⁾

The increase of oxidising potential accompanied with the increase of ferrous and manganeous oxides results to the growth of interlayer thickness and leads to a deterioration of the slag removal. However slag detachability was improved with the increase of TiO_2 content in coated-electrode. At that time the next combination of interlayer could be formed: M(Fe, Mn, V, Ti)O·TiO₂·n(Fe, Al, Cr)₂O₃. Further the importance of polymorphic transformation on $2CaO·SiO_2$ is emphasized to proceed detachability of slag in lime-fluorite type electrodes. ³⁶)

4. State Analysis of Titanium Ion in Slag

4.1 Infrared spectroscopy

Although the crystallization and transformation behavior of slag, SiO_2 -MnO- TiO_2 -CaF₂ system, by heating was studied with IR, X-ray diffraction and DTA, information concerning TiO_2 could not be found.³⁷⁾

With the comparison of standard frequencies of various titanates as given in Table 3, infrared emission spectra of molten slags of the system $\rm Na_2O\text{-}TiO_2\text{-}SiO_2$ was studied. The results obtained are as follows:

- (1) The remarkable difference of the IR spectra between the solidified and molten states could be determined.
- (2) With the increase of Ti⁴⁺ ion concentration, the intensities of 570 and 335 cm⁻¹ based on TiO₆⁸⁻ structure become stronger. It was concluded that Ti⁴⁺ ions almostly occupy the octahedral positions.
- (3) The formation of tetrahedral and pentahedral titanium ions could not be found.

Table 3 Frequencies of titanates obtained from the infrared, Raman and neutron data³⁸⁾

Structure	Frequency (cm ⁻¹)							Ref.	
	(LO)	(TO)		(LO)	(TO)				
(I) Infrared	:								
BaTiO ₃ (Tetragonal)		545			400				
BaTiO ₃ (Hexagonal)		555			365				
PbTiO ₃ (Tetragonal)		590			405				
SrTiO ₃ (Cubic)		610			395				Last ⁵⁶⁾
CaTiO ₃ (Orthorhombic)	700	540			360				
CdTiO ₃ (Ilmenite)		575		425	335				
BaTiO ₃ (Tetraginal)			491				182	174	Ballantype ⁵⁷⁾
BaTiO ₃ (Cubic)			491				182		
(II) Raman									
BaTiO ₃ (Orthorhombic)	718	519			309	245			
BaTiO ₃ (Tetragonal)	722	518			307	271			Perry et al. 58)
BaTiO ₃ (Cubic)		515				230			
PbTiO ₃		530		400		220	172	83	Ikegami ⁵⁹⁾
CaTiO ₃ (Orthorhombic)		549		443			179	148	
(III) Neutron									
BaTiO ₃ (Tetragonal)	780	450			340	235			
BaTiO ₃ (Cubic)	780	450			340	235			Pelah et al. ⁶⁰⁾
(I) Infrared									
Ba ₂ TiO ₄		720							Tarte ⁶¹⁾
(II) Raman									
Ba ₂ TiO ₄		745				250			Bobovich ⁶²⁾

(4) With the increase of TiO₂ content, Si-O⁻ fraction shows increament. From this evidence it will be anticipated that Ti⁴⁺ ions behave as modifier.

In Figure 13, the relative abundance of Si-O bond in the system Na₂O-TiO₂-SiO₂ is shown.³⁸⁾

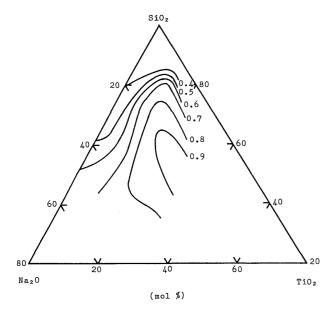


Fig. 14 The relative abundance of Si-O⁻ bond in the system Na₂-O-TiO₂-SiO₂³⁸)

4.2 Chemical analysis

The state of titanium ion in the slags of the system CaO-SiO₂-Al₂O₃-MgO equilibrated with graphite under the reduced atomosphere using CO gas was determined with chemical analysis.³⁹⁾ Results obtained are as follows:

- (1) The Ti⁴⁺ ion in slags is found to behave amphoterically with the critical CaO/SiO₂ ratio equal to unity.
- (2) The Ti³⁺ ion behaves basic except in highly basic slags such as in the CaO-Al₂O₃ system, where it turns out to behave acidic.

4.3 Electron spin resonance (ESR) and optical absorption analyses

The state of titanium ion in the slags of $Na_2O-SiO_2-TiO_2$ system under the reducing condition ($Po_2 = 2.1 \times 10^{-9}$ atm.) was investigated with ESR and optical absorption. ^{40),41)} The results obtained are as follows:

(1) An optical absorption with a shoulder was observed at 20,000 cm⁻¹. ESR absorption was also observed near g = 1.924. These observations were assigned to Ti³⁺ ions in octahedral environment with tetragonal distortion. (2) Based on the structural consideration of silicate slag, and redox reaction it is indicated that tetragonally and distorted environment arises from the octahedrally coordinations of free and non-bridged oxygens to Ti³⁺ ions, that is from Ti³⁺O₄-O₂²⁻ and Ti³⁺ O₅-O²⁻ units.

In Figure 15, ESR spectra of soda silicate slags containing $5.0 \, \text{mo} \, 1\%$ TiO₂ produced under reducing condition are shown.

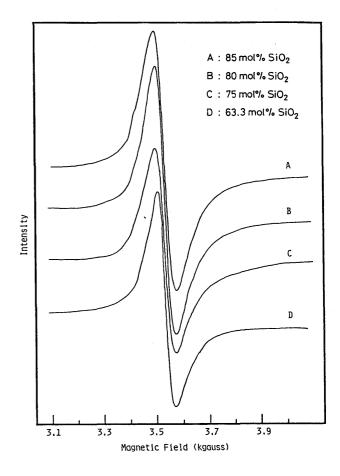


Fig. 15 ESR spectra of soda silicate slags containing 5.0 mo1% ${
m TiO_2}^{40}$)

Transfer of Titanium in Weld Metal from the Molten Slag Containing TiO₂

With the combined addition of titanium and boron in weld metal of $50\text{-}60\text{kg/mm}^2$ low alloy steels, mechanical properties such as notch toughness, COD, and yield and tensile strengthes can be improved. For that object it has been deveroped to introduce titanium and boron in weld metal by reducing TiO_2 and B_2O_3 contained in flux. $^{42}, ^{43}$

Titanium transfer from TiO₂ in the flux to the weld metal is influenced not only by the TiO₂ content but also the basicity of flux and the increase in partition rate from flux to weld metal can be obtained with increasing basicity and additions of metallic aluminium and magnesium.⁴⁴⁾

In Figure 16, the relation between titanium and the basicity of flux is shown. In this case the basicity value is based on the ratio of SiO₂/MgO with the constant content of TiO₂, CaF₂ and Al₂O₃. The transfer of titanium in weld metal shows the increament with the decrease of SiO₂ content in flux.

As other information the transfer of titanium is independent on CaF₂-content.⁴⁵⁾

In many papers, it is reported why titanium containing in weld metal gives good effect on toughness. 46)-55)

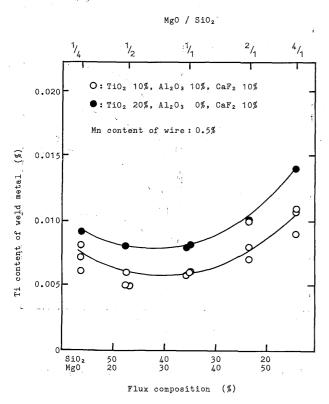


Fig. 16 The relation between titanium transfer in weld metal and the basicity of flux.

6. Summary

Although flux composition determines the mechanical properties of weld metal, individual role of additive in flux is not clear. In the welding metallurgy, the introduction of classical thermodynamics from metallurgy has been done, especially on the recovery of manganese and silicon in weld metal.

However, with the improvement of additives such as TiO_2 and CaF_2 , systematization of our thought concerning chemical reaction in molten slag and metal must be hasten. In this review, the role of TiO_2 in flux on elemental transfer in weld metal was summerized chiefly.

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