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Wetting Phenomena at High Temperature - Part 1

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Abstract

There are many wetting phenomena in metallurgical and welding fields. In this review, wetting phenomena relating to deoxidation process of liquid steel will be explained and the possibility of reducing non-metallic inclusions will be discussed from the viewpoint of interfacial control.

KEY WORDS : (Wettability) (Deoxidation) (Surface Tension) (Contact Angle)

1. Introduction

It is very important to understand the wetting phenomena in metallurgical and welding fields to obtain high quality and high performance materials. In this review, we will discuss the wetting phenomena at high temperature, since wetting phenomena at high temperature have to be taken into account not only physical interaction but also chemical interaction between liquid and solid. The systems which we will deal with here should be liquid metals, liquid oxides, solid metals, solid oxides, solid carbides and solid nitrides.

2. Why should we study and try to control the wetting phenomena in metallurgical and welding fields?

It is good for you to show some examples for the above question.

In deoxidation process of liquid steel, it is important to minimize oxide inclusions to obtain high quality steel. It is, of course, not difficult to remove large inclusions since the specific gravity of inclusions such as alumina, mullite and silica is sufficiently smaller than that of liquid steels. In the case of small inclusions (under 10 μm), however, they will suspend in liquid steel when liquid steel wet well inclusions. Accordingly, non-wetting systems are desired in the deoxidation process.

On the contrary, in a fabrication process of oxide dispersed steel, it is necessary for liquid steel to wet oxides.

These above mentioned examples suggest that it is not enough to study the wettability but necessary to control it.

3. definition of Wettability

As shown in Fig. 1, contact angle between liquid and solid can be used as an index of wettability because the contact angle can be easily measured by the sessile drop method. The contact angle, however, is not suitable for the index, when we want to demonstrate the wetting phenomena thermodynamically.

The work of adhesion, which is defined as the work required to separate liquid from solid, can be expressed as eq.(1)

$$W_{ad} = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \quad (1)$$

where, W_{ad} : the work of adhesion, γ_{sv} , γ_{lv} and γ_{sl} : the interfacial free energies between solid and vapor, liquid and vapor and solid and liquid, respectively.

The interfacial free energy between liquid and vapor (surface tension of liquid) can be measured precisely by the sessile drop method, the maximum bubble pressure method and so on. On the other hand, the interfacial free energy between solid and vapor is difficult to be measured and that between solid and liquid cannot be determined directly.

The relationship among these three interfacial free energies can be defined by Young's equation as shown in

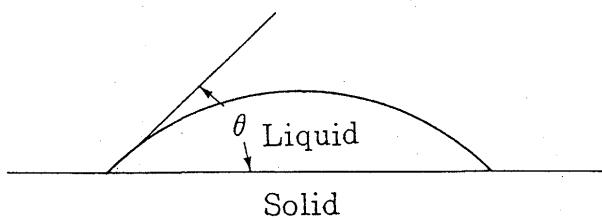


Fig. 1 Definition of contact angle of liquid on solid

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Fig. 2 and eq.(2)

$$\gamma_{sv} = \gamma_{lv} \cos \theta + \gamma_{sl} \quad (2)$$

Where, θ : the contact angle of liquid on solid.

Here, let's try to prove eq.(2) since many people might think eq.(2) is incorrect. The eq(2) should not be derived from a balance in forces, γ_{sv} , γ_{lv} and γ_{sl} but from free energy change at the equilibrium state.

As can be seen from **Fig. 3**, surface free energy change of a system can be described by the terms of surface area changes of liquid and solid and of interfacial area change between liquid and solid when the equilibrium contact angle, θ , changed slightly to $\theta + \delta \theta$. The change in the surface energy of the system, δF , can be denoted as:

$$\delta F = \gamma_{lv} \cdot \delta A \cdot \cos(\theta + \delta \theta) + \gamma_{sl} \cdot \delta A - \gamma_{sv} \cdot \delta A \quad (3)$$

Where, δA : surface and interface area change, $\delta \theta$: contact angle change

If we consider an indefinite small change, eq.(3) can be represented by:

$$\lim_{\delta \theta \rightarrow 0} (\delta F / \delta A) = \lim_{\delta \theta \rightarrow 0} (\gamma_{lv} \cdot \cos(\theta + \delta \theta) + \gamma_{sl} - \gamma_{sv}) = \gamma_{lv} \cdot \cos \theta + \gamma_{sl} - \gamma_{sv} = 0 \quad (4)$$

The eq. (4) corresponds to eq.(2).

The following equation can be derived from combination of eqs.(1) and (2).

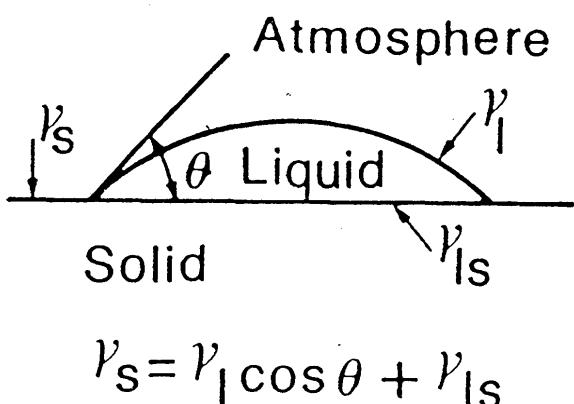


Fig. 2 Relationship between contact angle and interfacial free energies

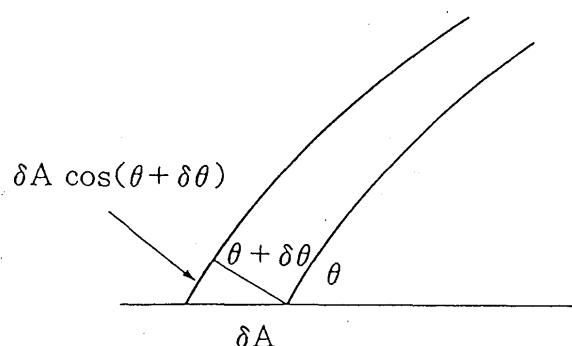


Fig. 3 Contact angle in equilibrium condition

$$Wad = \gamma_{lv} (1 + \cos \theta) \quad (5)$$

As mentioned above, γ_{lv} and θ are easy to be measured precisely by the sessile drop method. To compare the work of adhesion is useful to understand the wetting phenomena of different combinations of liquids and solids.

4. Wetting phenomena at high temperature

Several examples of metallurgical phenomena relating to wetting are shown in **Table 1**. It can be seen many combinations like as liquid metal / solid non-metal, liquid metal / solid metal, liquid non-metal / solid non-metal and liquid non-metal / solid metal systems. Many of them are classified by the following categories:

1. deoxidation process in steel making;
2. metal / ceramics joining;
3. fabrication of ceramic reinforced metal;
4. surface coating of oxide on metal - enameling;
5. brazing and soldering;
6. welding;

Now, we should know how important the wetting phenomena are in metallurgical and welding processes.

4.1 Deoxidation process in steel making¹⁾

In the steel making process the deoxidation of liquid steel is indispensable for the improvement of the quality of steel. Inclusions should be removed as possible as we can. Recently steel industries are paying attention to reduce small size inclusions suspended in liquid steel utilizing interface chemistry, that is, wettability. Here let's see how important the wettability is for refining the steel.

It is known that alumina which was formed by deoxidation of liquid steel with aluminum can be removed by adding a small amount of tellurium^{2,3)}.

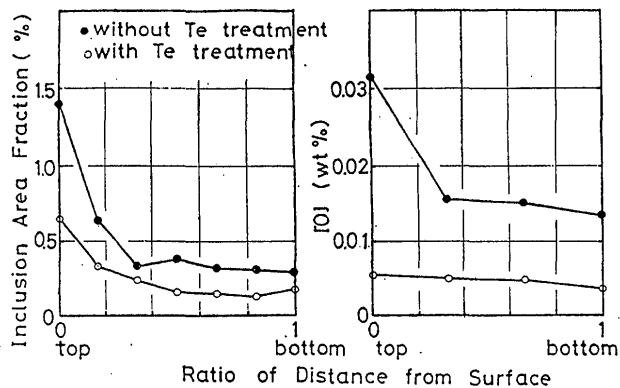
However, we could not clarify the reason why tellurium addition is effective to remove alumina inclusion. Two of the authors succeeded to explain the effect of tellurium by considering the effect of tellurium on the wettability of alumina by liquid steel¹⁾. Here, it will be described that the relationship between the effect of tellurium on the wettability of alumina by liquid steel and a degree of cleanliness of steel.

Figures 4 and 5 show the effect of tellurium addition on a distribution of inclusion in steel ingot 5 min. after Al addition. It can be seen from Figs. 4 and 5 that inclusion area fraction decreases significantly by tellurium treatment and the treatment is more effective near the surface of ingot than the bulk of ingot.

Figures 6 and 7 show the effect of tellurium on the surface tension of liquid steel and on the contact angle between alumina and liquid steel, respectively.

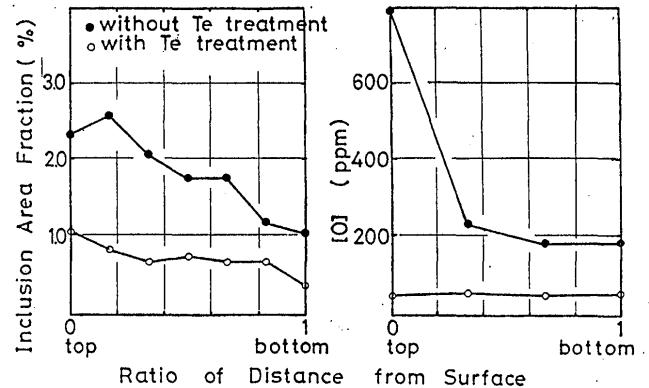
Table 1 Wetting phenomena in metallurgical and welding fields

Liquid	Solid	Related Phenomena
metal	oxide	reaction between liquid alloys and refractory deoxidation fabrication of metal matrix composites brazing joining
metal	metal	solidification welding surface coating casting fabrication of metal matrix composites powder metallurgy
metal	carbide	reaction between liquid alloys and refractory fabrication of metal matrix composites joining brazing
metal	nitride	fabrication of metal matrix composites joining brazing
oxide	metal	enamel coating ceramic coating
oxide	oxide	corrosion of refractory joining
oxide	nitride carbide	joining

**Fig. 4** Effect of tellurium on distribution of inclusions in center zone of ingot at 5 min. after aluminum addition

As can be seen from Fig. 6, the surface tension of liquid iron decreased dramatically as tellurium content increased in liquid iron. It is well known that oxygen and sulphur act as surface active elements in liquid metal. It can be concluded that tellurium, which belongs to the same group as oxygen and sulphur in the Periodic Table, is more surface active than them.

As is clear from Fig. 7, the contact angle of liquid iron on alumina increased significantly with an increasing of

**Fig. 5** Effect of tellurium on distribution of inclusions in surface zone (near interface between ingot and crucible) of ingot at 5 min. after aluminum addition

tellurium content. It has been reported that selenium also increases the contact angle between liquid iron and alumina and effect of tellurium is larger than that of selenium^{1,4)}.

The interfacial free energy and the work of adhesion between liquid and solid can be calculated from eqs. (1) and (2) if the surface tension and contact angle values were obtained. Of course, it is necessary to get the surface free energy value of solid for the calculation of

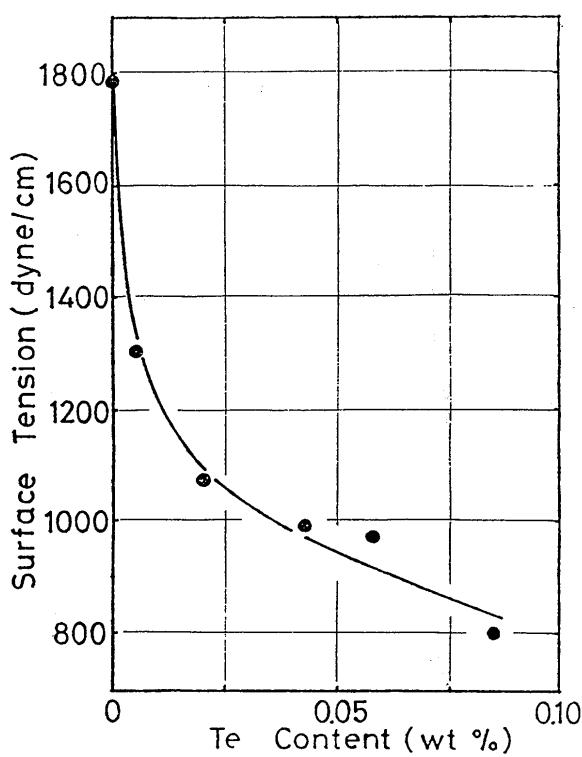


Fig. 6 Effect of tellurium on surface tension of liquid iron at 1873 K

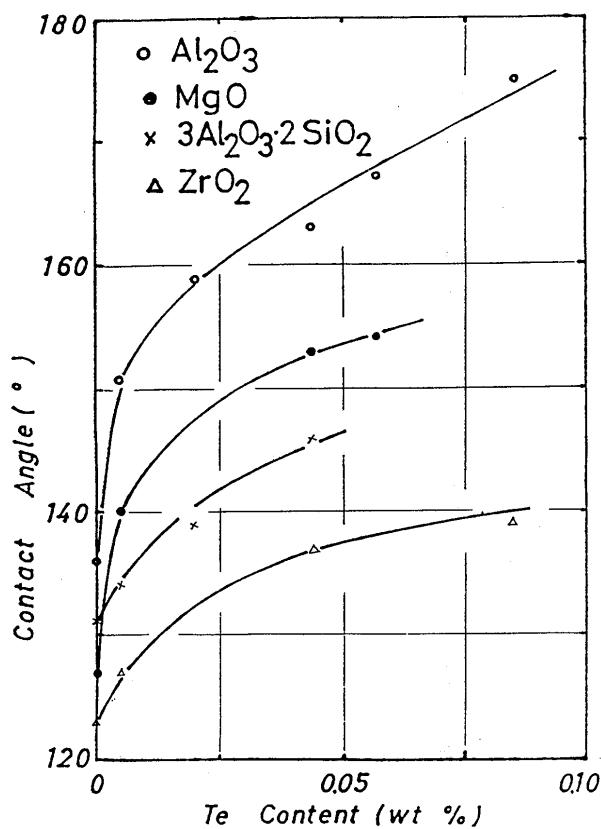


Fig. 7 Effect of tellurium on contact angle of liquid iron on various oxides at 1873 K

the interfacial free energy. The calculated values of them are shown in Figs. 8 and 9, respectively. Table 2 shows the surface free energy values for various oxides used for the calculation of the interfacial free energy. Even if the surface free energy value itself changed, the shape of curves Fig. 8 are not influenced at all.

As is clear from Figs. 8 and 9, the interfacial free energy and the work of adhesion decrease with an increasing of tellurium content in liquid iron.

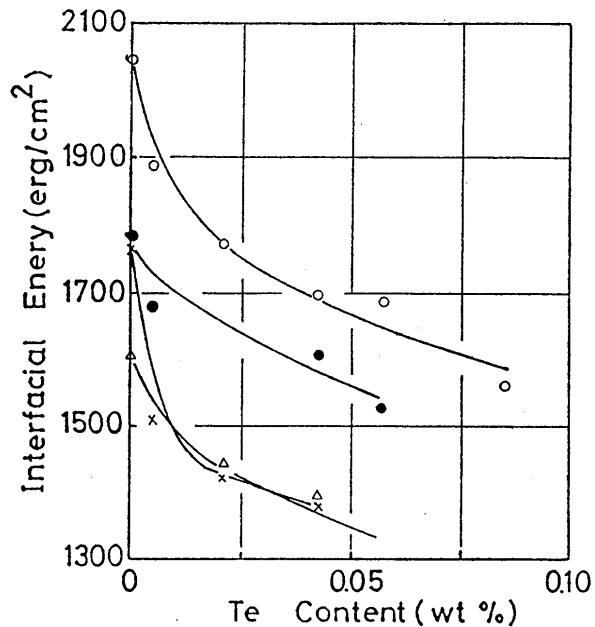


Fig. 8 Effect of tellurium on interfacial free energy between liquid iron and various oxides at 1873 K

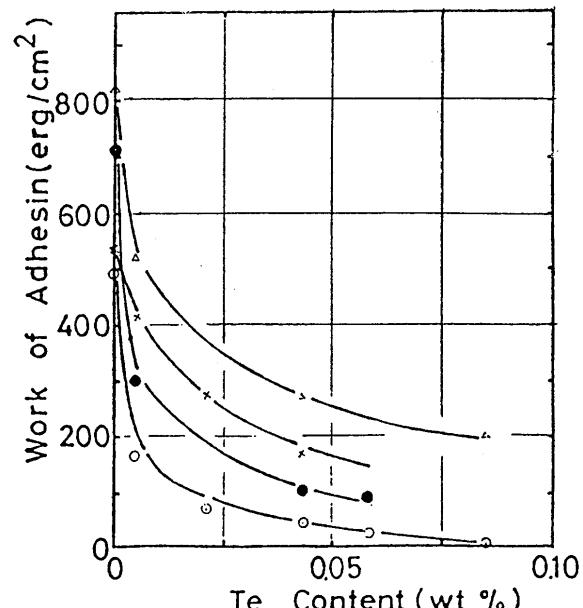


Fig. 9 Effect of tellurium on work of adhesion between liquid iron and various oxides at 1873 K

Table 2 Surface energy of solid oxides (erg·cm⁻²)

Oxide	Surface energy
Alumina	750
Magnesia	710
Zirconia	620
Mullite	500

The addition of tellurium was found to be effective for improvement of steel quality by reducing inclusions in the steel.

The effect of tellurium will be explained in terms of wetting phenomena. The deoxidation process of liquid steel can be broken down into five elementary stages as follows:

- (1) solution of deoxidizing agent in the bath;
- (2) nucleation of deoxidation products;
- (3) growth of nuclei;
- (4) rising up of deoxidation products;
- (5) elimination of deoxidation products from the bath.

These stages do not proceed step by step but overlap to a large extent. It can be considered that these stages, except for stage (1), are affected by the interfacial properties such as interfacial energy, work of adhesion, and contact angle. It is the purpose here to investigate them based on values of these interfacial properties.

4.1.1 Nucleation of deoxidation product

On the basis of the classical theory of nucleation demonstrated by Volmer and Webber, the free energy change of the formation of a spherical deoxidation product, ΔG , is represented by

$$\Delta G = 4\pi r^2 \gamma_{sl} - 4/3 \cdot \pi r^3 \Delta G_v \quad (6)$$

Where r : radius of deoxidation product (cm), γ_{sl} : interfacial free energy between liquid iron and deoxidation product (erg·cm⁻²), ΔG_v : volume free energy change of the formation of deoxidation product (erg·cm⁻²)

The critical radius r^* is that of the smallest deoxidation product which will grow spontaneously and can be

represented by

$$r^* = -2 \gamma_{sl} / \Delta G_v \quad (7)$$

Consequently, the energy which is necessary for this nuclei is

$$\Delta G^* = 16\pi \gamma_{sl}^3 / 3(\Delta G_v)^3 \quad (8)$$

While the rate of formation of nuclei per 1cm³ of liquid iron per second, I , can be defined by

$$I = A \exp(-\Delta G^*/(KT)) \quad (9)$$

Where K : Boltzmann's constant (1.381×10^{-16} erg/K), T : absolute temperature (K), A : frequency factor.

The degree of supersaturation, S^* , is represented by

$$S^* = -\exp(2.7 \cdot v/RT) \cdot (\gamma_{sl}^3 / (KT \log A))^{1/2} \quad (10)$$

The ratio of S^* with and without the addition of tellurium is shown in **Table 3**. It is clear from Table 3 that the addition of tellurium reduces the degree of critical supersaturation since the values of $\ln S^*/\ln S_{Te}^*$ for all of deoxidation products are from 1.25 to 1.37.

4.1.2 Growth of inclusion

Many ideas have been proposed for the growth of deoxidation products based on simplified assumptions and mechanisms are classified into two categories:

- (1) growth by diffusion;
- (2) cohesive growth by collision.

In the real system, the above two mechanism should occur but only the cohesive growth by collision will be discussed here since the interfacial properties between molten iron and deoxidation product have direct effects on the growth. Assuming that the cohesion of deoxidation products in the bath occurred by sintering originated from volume diffusion, the time, t , required for the sintering is represented by⁵

$$t = X^5 RT / r^2 K D_v \quad (11)$$

where, X : neck radius assumed to be $X = r/3$ (cm); K : the shape factor (10~100); D_v : the volume diffusivity (cm² sec⁻¹).

It has been reported that the time required for the sintering of alumina particles (2 μ m) is 15.8s and these inclusions are expressed to coalesce into clusters during their floatation⁶. We have found that except for the case of deoxidation with silicon and aluminum, the average

Table 3 Critical supersaturation necessary for homogeneous nucleation at 1873 K

Deoxidation product	Molar volume (cm ³ mol ⁻¹)	Interfacial energy (erg cm ⁻²)	$\ln S^*/\ln S_{Te}^*$
ZrO_2	23.2	1600 (without Te)	1.30
		1340 (with Te)	
$3Al_2O_3 \cdot 2SiO_2$	32.8	1750 (without Te)	1.37
		1420 (with Te)	
Al_2O_3	34.3	2050 (without Te)	1.27
		1750 (with Te)	

radius of deoxidation products was smaller than $2 \mu\text{m}$ and these radii decrease with the addition of tellurium. It was found from the observation by means of scanning electron microscopy that the average radius of alumina was $0.7 \mu\text{m}$ (without the addition of tellurium) and $0.4 \mu\text{m}$ (with the addition of tellurium) and that of zirconia $1.0 \mu\text{m}$ (without the addition of tellurium) and $0.5 \mu\text{m}$ (with the addition of tellurium).

By substituting the values of X and r obtained and D_v determined by Kucznski ($4.4 \times 10^{-12} \text{ cm}^2\text{s}^{-1}$)⁷⁾, into equation (8), the sintering times obtained are tabulated in Table 4. It is evident from Table 4 that the addition of tellurium promotes the growth of deoxidation products caused by cohesion.

The change in free energy, ΔG_{coh} , caused by cohesion of deoxidation products is represented by

$$\Delta G_{\text{coh}} = \gamma_{\text{ss}} - \gamma_{\text{sl}} \quad (12)$$

where γ_{ss} : the grain boundary energy of deoxidation products ($\text{erg}\cdot\text{cm}^{-2}$).

By assuming that $\gamma_{\text{ss}} = \gamma_{\text{sv}}$, the eq. (12) can be obtained.

$$\Delta G_{\text{coh}} = 2\gamma_1 \cos \theta \quad (13)$$

By substituting γ_1 in Fig. 6 and θ in Fig. 7 into equation (13), it can be obtained ΔG_{coh} of alumina is equal to $-2600 \text{ erg}\cdot\text{cm}^{-2}$ (without the addition of tellurium), $-2000 \text{ erg}\cdot\text{cm}^{-2}$ (with the addition of tellurium) and that of zirconia $-1950 \text{ erg}\cdot\text{cm}^{-2}$ (without the addition of tellurium), and $-1450 \text{ erg}\cdot\text{cm}^{-2}$ (with the addition of tellurium). All of these values are negative and the addition of tellurium is thermodynamically disadvantageous for the cohesion of deoxidation products. Nevertheless, the cohesion of deoxidation products proceeded as tellurium was added. This is caused by the small value of degree of supersaturation shown in Table 3 and the rapid sintering of deoxidation products with the addition of tellurium.

4.1.3 Floating up of deoxidation products

The rising velocity of deoxidation products in a quiescent bath has been given by

$$v = 2gr^2\Delta d/9\eta \cdot (3\eta + \beta r)/(2\eta + \beta r) \quad (14)$$

where v : rising velocity of deoxidation product ($\text{cm}\cdot\text{s}^{-1}$);

Table 4 Time required for the sintering of deoxidation product

Deoxidation product	Time(s)
Al_2O_3^*	7.8
$\text{Al}_2\text{O}_3^\dagger$	1.7
ZrO_2^*	38.0
ZrO_2^\dagger	8.5

* Without the addition of tellurium.

† With the addition of tellurium.

g : gravity ($980 \text{ cm}\cdot\text{s}^{-2}$) ; η : viscosity of liquid iron (poise) ; Δd : the difference in the density between liquid iron and deoxidation product ($\text{g}\cdot\text{cm}^{-3}$) ; β : frictional coefficient ($0 \leq \beta \leq \infty$) ($\beta = 0$ corresponds to the perfect slip, i.e. non-wetting ; $\beta = \infty$ corresponds to the perfect non-slip, i.e. wetting)

The interfacial properties contribute only to β and the ratio of rising velocities becomes $\beta = 0 / \beta = \infty = 1.5$. Equation (15) also has been obtained by considering the effect of the wettability of deoxidation product by liquid steel on the rising velocity⁸⁾.

$$v = 2/3 \cdot \eta^{-1} \cdot (r^2 \cdot g \cdot \Delta d/3 - (W_{\text{ad}} - 2\gamma_{\text{sv}})/\pi) \quad (15)$$

When the alumina particle ($r = 10^{-3} \text{ cm}$, $\Delta d = 3.13 \text{ g}\cdot\text{cm}^{-3}$, $\gamma_{\text{sv}} = 750 \text{ erg}\cdot\text{cm}^{-2}$) would rise up in liquid steel, the rising velocity becomes 1.42 times by the addition of tellurium. It is clear from eqs. (14) and (15) that the addition of tellurium promotes the rising up of deoxidation products but in the industrial process the effect of stirring may larger than that of tellurium.

4.1.4 Removal of deoxidation product from bath

As can be seen from Figs. 4 and 5 and Photo. 1, tellurium has been the most marked effect on this stage 5. Photograph 1 shows the appearance of the surface of ingots which were deoxidized with aluminum. Considerable differences were observed between those with and without the addition of tellurium. The ingot surface with tellurium treatment was covered with white powder which was confirmed to be α -alumina by the X-ray diffraction method. The amount of α -alumina which had been removed was about 0.3g corresponded to 60% of the initial oxygen content. The α -alumina powder, on the other hand, could not be observed on the surface of the ingot which had no addition of tellurium.

Few papers related to stage 5 have been presented from the view point of a surface chemical study, except for the papers which were presented by Kozakevitch et al⁹⁾ and by authors¹⁾.

The change in free energy caused by floating out of the plate-like deoxidation product is represented by⁹⁾:

$$\Delta G_{\text{rem}} = 2\gamma_{\text{sv}} + \gamma_{\text{lv}} - (\gamma_{\text{sv}} + \gamma_{\text{sl}}) = W_{\text{ad}} \quad (16)$$

Therefore in the case of alumina, ΔG_{rem} is $500 \text{ erg}\cdot\text{cm}^{-2}$

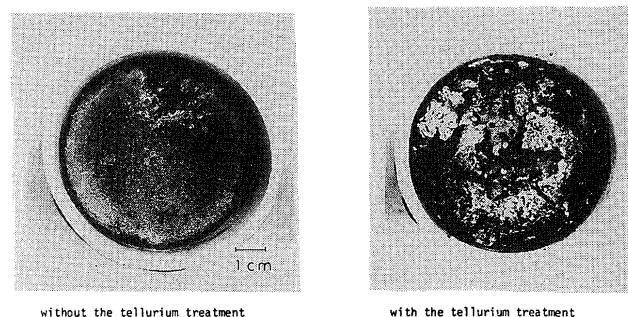


Photo. 1 Surface appearance of ingot at 5 min. after aluminum addition

(without the addition on tellurium) and 80 erg·cm⁻² (with the addition of tellurium) and that of zirconia is 820 erg·cm⁻² (without the addition of tellurium) and 380 erg·cm⁻² (with the addition of tellurium). Accordingly, ΔG_{rem} decreases with the addition of tellurium and the floating out of deoxidation products cannot occur spontaneously since these values are always positive even if the tellurium was added. But the elimination of deoxidation products was observed and it can be considered this is caused by the following factors;

- (1) convection of bath;
- (2) push-up effect of deoxidation products which rose up subsequently.

In the industrial process, as the strong convection are introduced by stirring, it is possible for the deoxidation products which rose up to the surface of the liquid iron to be caught into the bath again. But when the work of adhesion is small, the deoxidation products will be left on the surface of bath. This implies that the addition of tellurium is effective not only for deoxidation by aluminum but also that by other deoxidizers such as magnesium, zirconium and aluminum and silicon as you can see from Fig. 9.

In chapter IV, the interfacial properties such as contact angle, surface tension, work of adhesion and interfacial free energy were measured with the sessile drop method and the results of deoxidation of liquid steel with some deoxidizers were investigated from the view point of interfacial phenomena.

The following can be concluded:

1. the surface tension of liquid iron significantly decreased with the addition of tellurium.
2. the contact angles of liquid iron on alumina, magnesia, zirconia and mullite increased with the addition of tellurium.
3. the interfacial energy between liquid iron and alumina decreases with the addition of tellurium.
4. the work of adhesion between liquid iron and alumina decreased with the addition of tellurium.
5. the interfacial properties, especially the work of adhesion significantly affects on the degree of cleanliness of steel.

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(to be continued)