WETTING CONDITIONS IN STEEL / SLAG / GAS - SYSTEMS
AT 1550°C

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Experimental work has been carried out to measure the surface tension of liquid Armco iron at 1550°C with additions of the alloying elements and metalloids sulphur, manganese, silicon, carbon, chromium, nickel, vanadium, molybdenum, and titanium using the drop weight method. The interfacial tension between the metal phase and a molten slag composed of 40%CaO-40%SiO2-20%Al2O3 has been determined by the drop detachment method. From the knowledge of these values an assessment of the wetting conditions in the investigated steel/slag/gas-systems is possible. The results are presented by the wetting coefficient, the cosine of the wetting angle, and the work of adhesion between steel and slag.

INTRODUCTION

In the metallurgical processes, e.g. the converter processes and in gas injection of ladle treatment, the physical-chemical reactions are influenced by the interfacial tensions between the involved phases: steel, slag, and gas. The cleanliness of steel, or the suspension of metal droplets in the molten slag depend on the surface tension of steel and the interfacial tensions between steel and slag. From the knowledge of the interfacial energies the wetting conditions in steel/slag/gas - systems can be deduced. Principally film stability, flotation (emulsifying behaviour), and dispersion (phase separating behaviour) can occur resulting from the minimum free energy of interface.

Consider a gas bubble passing through the steel/slag phase boundary. In the case of film stability the bubble transports a closed steel film into the slag. In case of flotation this steel film disintegrates into droplets, which adhere more or less strongly to the bubble. Finally the droplets detach completely and are distributed within the slag. This happens in the case of dispersion.
EXPERIMENTAL

To investigate the wetting conditions in steel/slag/gas systems the surface tensions of different steel alloys and the interfacial tensions between these alloys and a synthetic slag of the composition 40%CaO-40%SiO₂-20%Al₂O₃ were determined experimentally at the Institute for Ferrous Metallurgy (IEHK) of the RWTH Aachen in Germany. The base material of the alloys was Armco iron, that, after a treatment by vacuum carbon deoxidation, was alloyed with the elements sulphur, manganese, silicon, carbon, chromium, nickel, vanadium, molybdenum, and titanium. The influence of each of these nine elements on the surface tension of steel and the interfacial tension between steel and slag was investigated separately by increasing its concentration in the steel at definite steps up to the maximum concentration mentioned in table I column two. The third column of table I indicates whether the element is surface active (+) or surface inactive (-). The order of elements from top to bottom corresponds to the surface activity in pure iron, see column four. The explanations of column four to seven are given at the results.

Table I. Investigated alloying elements and metalloids

| element | maximum mass contents in % | surface activity | F₀ pure iron calculated | F₀ Armco measured | interfacial activity | F₇ Armco measured |
|---------|---------------------------|------------------|------------------------|-------------------|---------------------|-------------------|
| S       | 0.29                      | +                | 150                    | 288.5             | +                   | 67.5              |
| Mn      | 4.27                      | +                | 3.6                    | 3.44              |                     |                   |
| Si      | 4.21                      | +                | 2.7                    | 2.71              | +                   | 3.21              |
| C       | 1.50                      | +                | 2.3                    | 2.56              | +                   | 4.44              |
| Cr      | 19.78                     | +                | 2.1                    | 1.82              | +                   | 2.07              |
| Ni      | 10.71                     | -                | 0.7                    | 0.77              | +                   |                   |
| V       | 3.99                      | -                | 0.81                   | +                 | 2.15                |                   |
| Mo      | 1.89                      | -                | 0.006                  | +                 |                     |                   |
| Ti      | 0.20                      | -                | 0.87                   | +                 | 33.2                |                   |

All tests were carried out in nitrogen atmosphere as gas phase and at a temperature of 1,550°C. The measurement of the surface tension of steel was carried out by the drop weight method and the interfacial tension between steel and slag by the drop detachment method. Both methods are based on a weight determination and yield good reproducible results (1,2,3). The slag was prepared from a prefused and homogenized
mixture of 40%CaO, 40%SiO₂, and 20%Al₂O₃. It has a melting point of 1,350°C and a surface tension of σₐ=0.468 N/m at the experimental temperature of 1,550°C (4).

In general, chemical reactions and element transfer between steel and slag reduce the interfacial tension. Therefore, a pre-condition of the interfacial tension measurement is that no chemical reaction or element transfer occurs between steel and slag. In the investigations with Mn, Si, C, Cr, Ni, V and Mo no changes of the chemical compositions of the steel and the slag were observed, the only exceptions being sulphur and titanium. These two elements react with the slag until a chemical equilibrium is established. To ensure that no such reactions take place sulphur or titanium oxide were added to the slag, up to the equilibrium concentration calculated by thermodynamic data (3).

RESULTS AND DISCUSSION

Provided there is a dynamic adsorption-desorption-equilibrium, the Langmuir adsorption isotherm of monolayer adsorption for the surface excess concentration Γ can be deduced:

$$\Gamma = \frac{z \cdot (F-1) \cdot x}{1 + (F-1) \cdot x} \quad [1]$$

where x is the molar bulk concentration of the alloying element or metalloid, z is the total number of adsorption sides, and F is a parameter characterizing the capillary activity of the element. Taking this into consideration, the integration of the Gibbs adsorption equation of dilute solutions:

$$\Gamma = -\frac{x}{R \cdot T} \cdot \frac{\partial \sigma}{\partial x} \quad [2]$$

yields an expression for the surface tension σ:

$$\sigma = \sigma_0 - z \cdot R \cdot T \cdot \ln(1 + (F-1) \cdot x) \quad [3]$$

where σ₀ is the surface tension of the base material. For Armco iron at 1,550°C it is σ₀,Armco=1.520 N/m. The symbols R and T stand for the gas constant and the temperature. The total number of adsorption sites in Armco iron is estimated to be z=5.71•10⁵ Mole/m² for the surfactants and z=3.619•10⁻⁴ Mole/m² for surface inactive elements. Table I column four gives the capillary activity parameters of the investigated elements in pure iron, F₀,pure iron, calculated by Shishkovsky (5).

The measured capillary activity parameters in Armco iron, F₀,Armco, are listed in table I column five. Note that, for the surface active elements S, Mn, Si, C, and Cr the
capillary activity parameter $F$ is greater than 1, and for the surface inactive elements Ni, V, Mo, and Ti it is less than 1. Generally the measured capillary activity parameters of the investigated elements in Armco iron are in the order of the values of pure iron, except the value of sulphur. The capillary activity parameter of sulphur in Armco iron exceeds the value in pure iron by a factor of 1.9. Among the surface active elements, sulphur reduces the surface tension the most.

All elements investigated decrease the interfacial tension between steel and slag, except manganese, which shows a varying influence at different concentrations, see table I column six. Furthermore, as an approximation the measured interfacial tensions in the experiments with S, Si, C, Cr, V and Ti may be represented by a relation analogous to equation 3. The resulting capillary activity parameters of the elements in the approximately interfacial tension calculations, $F_{y, \text{Armco}}$, are listed in table I column seven. As an example Figure 1 presents the measured and calculated interfacial tensions for S, Si, C, Cr, V, and Ti. In spite of sulphur being the most interfacial active element investigated, titanium reduces the interfacial tension between steel and slag significantly at low concentrations, too. At 1,550°C the interfacial tension between Armco iron and the 40%CaO-40%SiO$_2$-20%Al$_2$O$_3$ slag is $\gamma_{0, \text{Armco}}=1.335$ N/m. Note, that $\gamma_0-\gamma$ is a positive number in case of decreasing interfacial tension between steel and slag.

The wetting conditions of steel/slag/gas - systems are given completely by the three physical quantities: surface tension of slag $\sigma_S$, surface tension of steel $\sigma_M$ and interfacial tension between steel and slag $\gamma$. If these values are known, the wetting coefficient $p$ can be calculated from:

$$p = \frac{\sigma_M - \sigma_S}{\gamma}$$  \hspace{1cm} [4]

As mentioned at the introduction in metallurgical systems the different wetting conditions are usually classified as follows:

a) If the wetting coefficient is less than $-1$, the surface tension of the slag is higher than the sum of the interfacial tension and the surface tension of the steel, and film stability occurs.

b) In case of flotation the values of the wetting coefficient are in the range between $-1$ and $1$, and the absolute value of the difference between the surface tension of the steel and the surface tension of the slag is lower than the interfacial tension.

c) If the wetting coefficient exceeds the value $1$ the surface tension of the steel is higher than the sum of the interfacial tension and the surface tension of the slag. This happens in the case of dispersion.
The initial system of Armco iron/slag/gas has a wetting coefficient of $p_0=0.788$. This value is reduced by the additions of surface active elements and it is increased by alloying surface inactive elements. The wetting coefficients of all investigated steel/slag/gas-systems are in the range between 0.6 and 1.1. The measured wetting coefficients show, that the metallurgical systems are located far from the range of film stability in the range of flotation, and near the boundary between flotation and dispersion. Figure 2 shows a statistical relation between the two terms of the wetting coefficient, i.e. $\sigma_M/\gamma$ and $\sigma_S/\gamma$. The different symbols stand for the different experimental series for S, Mn, Si, C, Cr, Ni, V, Mo, and Ti. The diagram is divided into three parts, the area of film stability grey shaded at the top, the area of flotation in the middle, and the area of dispersion at the bottom. In the interests of clarity the concentrations are not depicted. The concentrations of the surface inactive elements Ni, V, Mo, and Ti move from left to right, and vice versa for the surface active elements S, Mn, Si, C, and Cr. Note, that all investigated systems are located in a well defined, nearly horizontal scatter band. The systems with the surface inactive elements titanium, molybdenum and vanadium move into the direction of dispersion, crossing the dividing line between flotation and dispersion at $\sigma_M/\gamma=1.4$.

The definition of the wetting angle is given in figure 3. It shows a drop of liquid slag floating on liquid steel. The three tensions constitute the Neumann triangle representing the balance of forces at the point of three-phase contact. The cosinus of the wetting angle can be calculated by the inserted equation. Complete wetting, i.e. spreading of the slag droplet to a thin film, is achieved if the wetting angle equals 0 or the cosinus of the wetting angle equals 1. For the investigated metallurgical systems there exists a linear relation between the cosinus of the wetting angle and the quotient of the work of adhesion versus surface tension of the slag $W_{ad}/\sigma_S$, see figure 4. As a comparison the Young-Dupré relation, which is valid in solid/liquid/gas-systems, is also depicted by a bold straight line. Complete wetting of steel and slag can appear with steels of a high contents of surface inactive alloying elements, such as vanadium and titanium. The concentrations move analogous to figure 2.

**CONCLUSIONS**

The surface tension of steel as a function of the concentrations of the alloying elements and metalloids S, Mn, Si, C, Cr, Ni, V, Mo and Ti can be calculated by the Langmuir adsorption isotherm of monolayer adsorption. All these elements are interfacial active except Mn. The investigated steel/slag/gas-systems are located in the range of flotation, near the boundary between flotation and dispersion. Systems with Ti, Mo or V move into the direction of dispersion. Furthermore, the systems exhibit a linear relation between the cosinus of the wetting angle and the quotient of the work of adhesion versus surface tension of the slag, similar to the Young-Dupré relation, which is valid in solid/liquid/gas-systems.
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