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Abstract

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THE EFFECT OF SULFUR ON THE INTERFACIAL TENSION AT THE METAL-SLAG BOUNDARY

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The study of the surface activity of sulfur is of substantial interest both for elucidating the mechanism of desulfurization of liquid steel and in considering the precipitation of sulfide inclusions during crystallization ([1,2]).

However, the effect of sulfur on the interfacial tension (σ) at the iron–slag boundary has not been studied. The only known work is that of Kazakevich and coauthors ([3]), in which the change in interfacial tension was determined during the transfer of sulfur from cast iron into an industrial slag. The authors concluded that σ increases in this case, and that under equilibrium conditions sulfur is inactive with respect to the interfacial boundary.

To study the behavior of sulfur with respect to the steel–slag interface, we adopted essentially the previous method ([4]). In contrast to it, in the present work an RUP-1 X-ray unit (200 kV) was used for radiographing the melt.

The metallic phase was technically pure iron, which was preliminarily fused in the required proportion with chemically pure FeS.

The slags were prepared from chemically pure oxides CaO, SiO_2, Al_2O_3, and Fe_2O_3 and contained:

	CaO	SiO_2	Al_2O_3	FeO	MgO
slag No. 1 (ferruginous)	34.9	34.6	–	27.2	0.5
slag No. 2 (blast-furnace)	47	27	23	1.0	0.1

With the ferruginous slag the experiments were carried out in crucibles machined from fused magnesia; with the blast-furnace slag, in corundum and graphite crucibles. In the latter case, to eliminate carburization, the metal drop was placed on a plate of MgO. Owing to interaction with the crucible and lining material, the content of magnesium oxide in the slags increased, reaching 11% by the end of the experiment. As the experiments showed, this had no substantial effect on the interfacial tension.

In some experiments sulfur was introduced only into the slag (in the form of FeS), in others into the metal, and in still others into both phases, in order to study not only the equilibrium but also the dynamic tension during the transfer of sulfur both from the metal into the slag and in the reverse direction.

The drops were photographed after melting of the metal every 10 min, while at the same time, by freezing on, a slag sample (about 2 g) was taken for determination of the sulfur concentration. In all experiments the weight of the metal drop was 11 g, while that of the slag varied from 30 to 50 g.

The establishment of equilibrium was determined from the constant sulfur content in the slag. It was usually reached after 15-20 min and coincided with the establishment of an unchanged drop shape. The magnitude of the dynamic tension was judged from individual photographs of the drops, comparing them with the subsequent equilibrium ones. Photographs of the drops were enlarged by about 6 times, and

from them, with the aid of a micrometric grid (division value 0.1 mm), the true dimensions were found. The relative error in their determination did not exceed 3%.

The values of the densities of the liquid slag required for the calculations were found experimentally (^{6}), and those for steel were taken from a handbook (^{7}).

The experiments showed that, at a low sulfur content in both phases, the interfacial tension at the boundary of iron with slag No. 1 is 650 erg/cm^2. With an increase in the sulfur concentration, the static interfacial tension decreases. The photographs of drops in Fig. 1 (the first and second vertical rows) may serve as a qualitative illustration of this. The numerical values

Fig. 1. Change in the shape of a metal drop with increasing sulfur concentration:

	S_{met} (a)	S_{met} ( )	S_{met} ( )	slag
1	0.025	0.90	3.4	No. 1
2	0.70	2.0	3.0	No. 1
3	0.025	0.17	0.5	No. 2

σ as a function of the sulfur content in the metal are given in Fig. 2. Its concentrations in slag No. 1 were approximately 1.6 times lower.

When the content of ferrous oxide in the slag is insignificant (slag No. 1), the interfacial tension at its boundary with iron ($[S]_{\text{met}} \approx 0.025\%$) is 1015 erg/cm^2. This differs little from the value obtained earlier at other concentrations of CaO, SiO_2, and Al_2O_3 (^{5}), and substantially exceeds the value of σ for ferruginous slag. With the introduction of sulfur, the static interfacial tension regularly decreases also for blast-furnace slag (see Fig. 1, third row, and Fig. 2), reaching, at 2% S in the metal

$$\left(\frac{S_{\text{slag}}}{S_{\text{met}}} \approx 2\right)$$

a value of 500 erg/cm^2.

Thus, sulfur substantially lowers the static interfacial tension of iron at the boundary both with oxidizing slag and with blast-furnace slag. In work (^{3}) this effect was not detected, apparently because the concentration of sulfur in the cast iron was low and changed little from one experiment to another.

The dynamic values σ_{dyn} in our experiments, as in work (^{3}), proved to be lower than the static ones. For example, in one of the experiments, during the transfer of sulfur from slag No. 2 into the steel, $\sigma_{\text{dyn}} = 470$ erg/cm^2, whereas at equilibrium $\sigma = 515$ erg/cm^2. In another experiment, during the transfer of S into slag No. 1, $\sigma_{\text{dyn}} = 440$ erg/cm^2, and at equilibrium 510 erg/cm^2.

The decrease in interfacial tension with increasing concentration of S is easy to understand if one takes into account that sulfur has high surface activity with respect to the steel-gas interface (^{8,9}). Being displaced into the surface layer of the metal, it binds rather strongly with the nearest slag cations, which accounts for the low values of σ. The weaker effect of sulfur in the case of ferrous slags is apparently connected with the increased concentration of oxygen in the metal, whose surface activity is close to that of sulfur (^{8,10}). Concentrating in the surface layer, oxygen partially displaces sulfur from it. Moreover, comparison of the strengths of sulfides and oxides suggests that the bond of oxygen with slag cations is stronger than that of sulfur. The circumstances noted—namely, the displacement of oxygen into the surface layer and its stronger bond with slag cations—cause a substantial lowering of the interfacial tension when oxygen is present in the metal and a weaker change in σ upon addition of sulfur.

Fig. 2. Effect of sulfur on the steel-slag interfacial tension at 1530-1570°: a —slag No. 1, b —slag No. 2

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In the absence of equilibrium, the directed transfer of sulfur across the phase boundary apparently blurs it, and in connection with this the dynamic tension is lower than the static tension.

The decrease in interfacial tension noted above with increasing concentration of sulfur and oxygen indicates the greater thermodynamic stability of nonmetallic inclusions in steel when they contain high amounts of sulfur and ferrous oxide. In addition, adsorption of O and S may substantially change the magnitude of the disjoining pressure that prevents the coalescence of such emulsions (^{11}).

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