

The Effect of Zirconium, Cerium, and Lanthanum on the Solubility of Oxygen in Liquid Iron

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The effect of zirconium, cerium, and lanthanum up to about 1 wt pct on the solubility of oxygen in liquid iron in equilibrium with an oxide phase at 1680°C was measured. All three elements are strong deoxidizers of iron, and the oxygen solubility minimums were 10 ppm or less at 0.05 to 0.1 wt pct of the alloying element. The interaction coefficients were estimated from the results giving $e_{\text{O}}^{\text{Zr}} = -3$, $e_{\text{O}}^{\text{Ce}} = -3$, and $e_{\text{O}}^{\text{La}} = -5$. When the concentration of the alloying element is expressed in wt pct, the effect of each of the three elements (Zr, Ce, and La) on the activity and solubility of oxygen in liquid iron is similar to that of aluminum.

THE effects of most of the common alloying elements in steel on the solubility of oxygen in liquid iron are known; recently Turkdogan¹ reviewed much of this information. However, there are several alloying elements for which little is known about their effects on the solubility of oxygen in iron, in particular zirconium, cerium, and lanthanum. These three elements appear to be strong deoxidizers of steel, and the rare earths (Ce and La) have been used with CaO for improved desulfurization. It was the purpose of the present work to determine the solubility of oxygen in iron containing up to about 1 wt pct Zr, Ce, or La and the deoxidation constants for these elements. The effect of the alloying elements on the activity coefficient of oxygen at low concentrations of the alloying elements was also estimated.

EXPERIMENTAL WORK

It proved necessary to make each alloy first in an induction furnace before equilibrating it in a resistance furnace. Initially, experiments were attempted in which a master alloy containing about 1 pct Zr was melted along with vacuum carbon deoxidized electrolytic iron in a resistance furnace. However, even after 2 h at 1680°C the resulting melts were not homogeneous. Apparently, the master alloy developed an oxide layer which suppressed the diffusion of Zr throughout the melt. Making each alloy in an induction furnace ensured a homogeneous melt. However, the solidified samples at this point contained suspended oxide particles. Therefore, the samples had to be remelted in a resistance furnace to allow the oxide particles to float out. Approximately 60 g of the alloy contained in a refractory boat (1.2 by 1.2 by 6 cm) was heated in a carbon resistance furnace to $1680 \pm 10^\circ\text{C}$ and allowed to equilibrate for about 2 h. On the basis of previous work,¹ 2 h should be more than sufficient time to allow all the oxides to float out; when samples were equilibrated for longer times, there was no significant difference in the results. The samples were cooled rapidly (15°C/min) in the furnace. A flowing atmosphere 100 ml/min of He was used during the experiments and the temperature was measured with a 5 to 20 Pt-Rh thermocouple. The samples were analyzed chemically for Zr, Ce, or La and for oxygen by neutron activation.

During the equilibration period in the resistance furnace the concentration of oxygen and of the alloying element (Zr, Ce, or La) decreased. For example, an Fe-Zr alloy made in the induction furnace contained 0.62 pct Zr and 70 ppm oxygen; after equilibration it contained 0.54 pct Zr and 28 ppm oxygen. The decrease in the oxygen content is due to the flotation of the oxide particles (ZrO_2) out of the melt, whereas the decrease in Zr is due to the oxide flotation and to further oxidation of the Zr.

The Fe-Zr alloys were melted in boats constructed of $\text{ZrO}_2 + 4$ pct CaO. The Fe-Ce and the Fe-La alloys were melted in ThO_2 , Al_2O_3 , and ZrO_2 boats. There was no significant difference in the results obtained when the different refractory materials were used, and there was no significant attack of the refractories. The Fe-Zr melts were in equilibrium with the ZrO_2 boat. In several experiments with the Fe-Ce and Fe-La alloys, CeO_2 or La_2O_3 was added initially with the metal sample to ensure that there was an equilibrium oxide phase present. However, when no extra oxide was added the results were essentially the same, indicating that there was sufficient oxide present or formed during the equilibration period to ensure that the equilibrium oxide phase was present.

RESULTS AND DISCUSSION

The experimental results are presented in Table I and plotted in Figs. 1 to 3 as $\log [\text{O}]$ (ppm) vs \log (wt pct Zr, Ce, or La). In Fig. 1 for Zr the limiting slope at low Zr concentrations is shown to be $-\frac{1}{2}$, indicating that the equilibrium phase is ZrO_2 . There is no direct evidence that ZrO_2 is the equilibrium oxide; however, ZrO_2 is the only reported oxide of Zr and the experimental data fit the line with a slope of $-\frac{1}{2}$ reasonably well. The solubility of oxygen is a minimum of 8 ppm at 0.08 pct Zr at 1680°C. A comparison with the minimum of about 8 ppm found in Fe-Al alloys at 1600°C at 0.1 wt pct Al^2 indicates that Zr is about as strong a deoxidizer of iron as aluminum.

Figs. 2 and 3 are similar plots for Ce and La, respectively. The limiting slope for Ce is $-\frac{1}{2}$ and for La is $-\frac{2}{3}$, indicating that the equilibrium oxide phases are CeO_2 and La_2O_3 , respectively. Again this is only indirect evidence of the composition of the equilibrated phase. Both elements are strong deoxidizers of liquid iron, with solubility minima of about 10 ppm at 1650°C. It appears that La may be a slightly stronger deoxidizer and reach the minimum oxygen content at a lower

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Table I. Experimental Results; Solubility of Oxygen in Iron Containing Zr, Ce, or La in Equilibrium With an Oxide Phase at 1680°C

Zr, wt pct	O, ppm	Crucible Material	Ce, wt pct	O, ppm	Crucible Material	La, wt pct	O, ppm	Crucible Material
0.005	28	ZrO ₂	0.002	54	ZrO ₂	0.002	50	ZrO ₂
0.008	23	ZrO ₂	0.004	35	Al ₂ O ₃	0.004	24	ThO ₂
0.011	22	ZrO ₂	0.005	34	ThO ₂	0.010	6	ThO ₂
0.019	14	ZrO ₂	0.019	13	ThO ₂	0.058	11	ZrO ₂
0.029	13	ZrO ₂	0.058	12	Al ₂ O ₃	0.20	25	ZrO ₂
0.074	6	ZrO ₂	0.11	11	ZrO ₂	0.20	50	ZrO ₂
0.15	11	ZrO ₂	0.49	30	ZrO ₂	0.65	107	ZrO ₂
0.23	46	ZrO ₂	0.80	50	ZrO ₂	-	-	-
0.39	44	ZrO ₂	-	-	-	-	-	-
0.54	23	ZrO ₂	-	-	-	-	-	-
0.10	62	ZrO ₂	-	-	-	-	-	-

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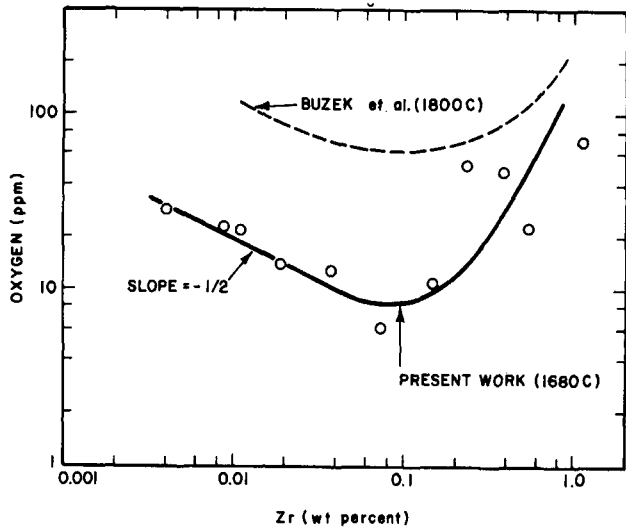


Fig. 1—Solubility of oxygen in Fe-Zr alloys at 1680°C.

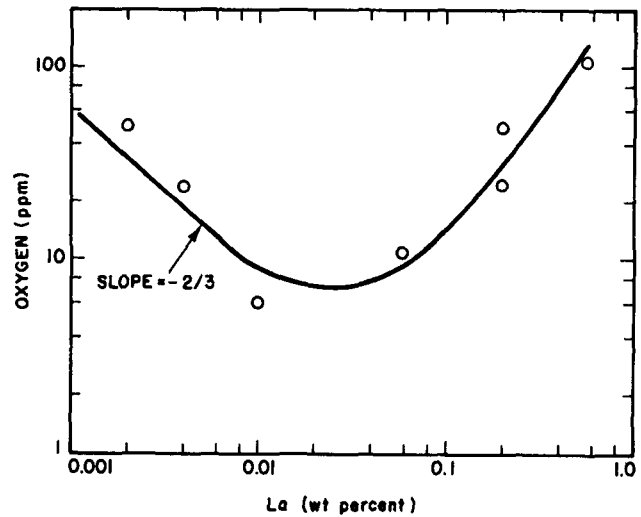


Fig. 3—Solubility of oxygen in Fe-La alloys at 1680°C.

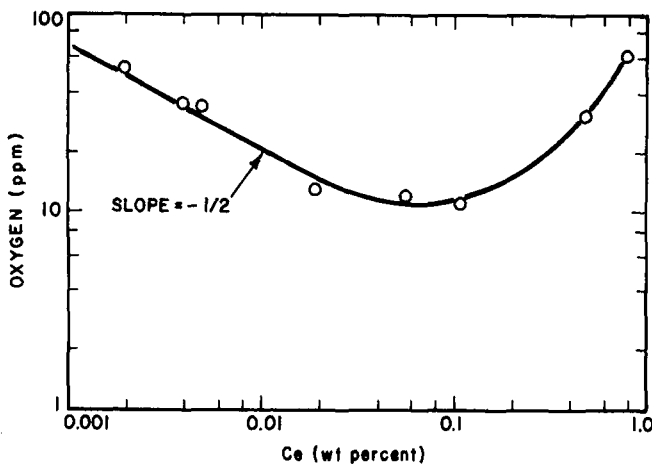


Fig. 2—Solubility of oxygen in Fe-Ce alloys at 1680°C.

concentration of the alloying element.

A convenient way of expressing deoxidation reaction is by means of the deoxidation product (K'_j)

$$K'_{Zr} = (\text{wt pct Zr})(\text{wt pct O})^2 \quad [1]$$

$$K'_{Ce} = (\text{wt pct Ce})(\text{wt pct O})^2 \quad [2]$$

$$K'_{La} = (\text{wt pct La})^2(\text{wt pct O})^3 \quad [3]$$

The values of the deoxidation products are plotted vs composition in Fig. 4, and the limiting values of the deoxidation products at infinite dilution of the alloying

element (K_j^O) are listed in Table II. For convenience and clarity the values of K'_j obtained below 0.05 wt pct of the alloying elements are averaged into a single point in Fig. 4. The deoxidation products at infinite dilution (K^O) are equilibrium constants since the activities of the components are proportional to their concentrations at infinite dilution.

The activity of oxygen was not measured directly; however, it is possible to estimate the interaction coefficients e_O^j from the compositional dependence of K_j .

$$e_O^j = \left(\frac{d(\log f_O)}{d(\text{wt pct } j)} \right)_{j \rightarrow 0} \quad [4]$$

where f_O is the activity coefficient of oxygen in the alloy relative to that in unalloyed iron. The technique used to estimate the values of the interaction coefficients is subject to error and the values obtained should be considered rough estimates only. However, since no reliable values exist, their estimation is of some value.

Assuming that first-order interaction coefficients can adequately describe the thermodynamics of the system, the following equation can be written for the Fe-Zr-O system.

$$\log K'_{Zr} = \log (\text{pct Zr}) + 2 \log (\text{pct O}) \quad [5]$$

$$\log K'_{Zr} = \log a_{Zr} + 2 \log a_O - \log f_{Zr} - 2 \log f_O \quad [6]$$

$$\log K'_{Zr} = \log K'_{Zr}^O - e_{Zr}^{Zr} (\text{pct Zr}) - 2e_O^{Zr} (\text{pct Zr}) \quad [7]$$

where a_{Zr} and a_O are the activities relative to 1 wt pct.

Table II. Thermodynamic Parameters for Fe-Zr-O, Fe-Ce-O, and Fe-La-O Alloys at 1680°C

Alloying Element	K_f^o	e_o^j	ϵ_o^j
Zr	3.5×10^{-8}	-3	600
Ce	3.5×10^{-8}	-3	1800
La	2.5×10^{-13}	-5	3000

$K_{Zr}^o = (\text{pct Zr})(\text{pct O})^2$
 $K_{Ce}^o = (\text{pct Ce})(\text{pct O})^2$
 $K_{La}^o = (\text{pct La})^2(\text{pct O})^3$
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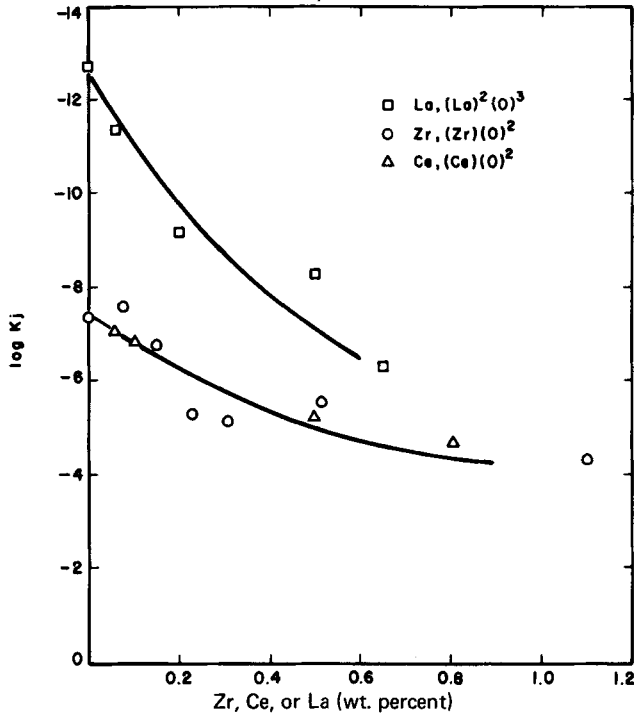


Fig. 4—The deoxidation products for Zr, Ce, and La in liquid iron at 1680°C.

For a strong deoxidizer like Zr, Ce, or La it is reasonable to assume that $e_{O}^{Zr} \gg e_{Zr}^{O}$; therefore the limiting slope of the line as wt pct Zr \rightarrow O in Fig. 4 is equal to $-2e_{O}^{Zr}$. A similar technique was used to estimate e_{O}^{Ce} and e_{O}^{La} . The values of e_{O}^{Zr} , e_{O}^{Ce} , and e_{O}^{La} computed in this manner and the values of the interaction coefficients in terms of mole fraction, ϵ_{O}^j , are listed in Table II.

$$\epsilon_{O}^j = \left(\frac{d \ln (\gamma_{O} / \gamma_{O}^0)}{dN_j} \right)_{N_{Fe} \rightarrow 1} \quad [8]$$

It should be stressed that computing interaction coefficients in this manner may be subject to significant error, as discussed in a previous publication.² In particular, the assumption that first-order interaction coefficients describe the thermodynamics may not be valid, except for the limiting case of infinite dilution.

As mentioned earlier, very little previous work has been done on the effect of Zr, Ce, or La on the solubility of oxygen in liquid iron. Buzek and Ostrova³ measured the solubility of oxygen in Fe-Zr melts at 1800°C. There was considerable scatter (± 25 ppm O) in their results; therefore, their results are approximated by the dashed line in Fig. 1. Their results are consistent with the present work considering the higher tempera-

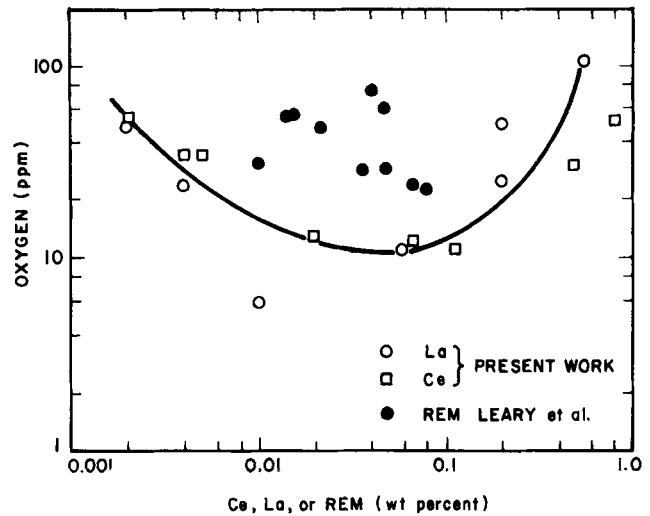


Fig. 5—Effect of rare earths on the solubility of oxygen in liquid Fe.

ture of their investigation. The value of K_{Zr}^o computed from their experimental results at 1800°C is 1.5×10^{-8} . Using a method similar to that employed in the present work, Buzek and Ostrova estimated $e_{O}^{Zr} = -4$ at 1800°C which compares reasonably well with the present estimate.

The most extensive study on the deoxidation of steel by rare earths was made by Leary *et al.*⁴ who determined the effect of addition of an "REM" alloy on the solubility of oxygen in steel. The major elements in the REM alloy in wt pct were cerium 48 to 50, lanthanum 32 to 44, and neodymium 5 to 8. They conducted tests on 1-ton heats melted in an arc furnace. Their results are given in Fig. 5; REM represents the total rare earth in the final ingot. They found oxygen contents somewhat higher than those in the present study, which is not surprising since they analyzed for total oxygen and there may have been entrapped oxide inclusions in the ingot. However, their results did indicate that the rare earths are strong deoxidizers, which is in agreement with the present work. Kusakawa and Watanabe⁵ made a few measurements on the solubility of oxygen in Fe-Ce-0.3 C alloys at 1600°C and found an oxygen solubility of about 20 ppm at 0.1 wt pct Ce, which is consistent with the present work.

CONCLUSIONS

Zirconium, cerium, and lanthanum are strong deoxidizers which lower the activity and solubility of oxygen in liquid iron in much the same way as aluminum. In the presence of 0.05 to 0.1 wt pct of these deoxidizers, the solubility limit for oxygen is about 10 ppm. The interaction coefficients (e_{O}^j) are estimated to be within the range -3 to -5.

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