The Determination of Chromium-Oxygen Interactions in Levitated Iron Alloy Droplets*

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Synopsis

The dissolution of oxygen in liquid iron and iron-chromium alloys has been investigated by means of a levitation melting procedure. The oxygen potential of the system was controlled with H_2/H_2O and CO/CO_2 gas mixtures. With H_2/H_2O and liquid iron, thermal diffusion effects are significant and results obtained at steady state should not be used to determine equilibrium constants directly. With CO/CO_2 , the steady state data are in closer agreement with published equilibrium values. Despite the existence of thermal diffusion it has been shown that the levitation technique can be employed to establish the relative effect of one element on the chemical behaviour of another. The influence of up to 24wt% chromium on the activity coefficient of oxygen in liquid iron has been determined for temperatures between 1550° and 1750°C. Interaction parameters from H_2/H_2O experiments were in good agreement with the values obtained using CO/CO_2 . While comparison with published data for several gas/metal and slag/metal studies indicates reasonable agreement, the inter-action effects appear to be much stronger than those measured using lime-stabilized zirconia cells.

I. Introduction

There have been a number of investigations which describe the effect of chromium on the behaviour of oxygen dissolved in liquid iron.¹⁻¹⁴ Much of the work, however, has been confined to chromium levels below 12wt% and to temperatures in the vicinity of 1600°C. All of the studies have been performed using oxide crucibles and frequently the melts have been saturated with respect to one of the oxides of chromium. Under these conditions it is not always possible to ensure that samples taken for oxygen analysis are free from entrapped oxides and hence representative of the original melt composition. In the present study, problems associated with melt contamination from crucible material and oxide solubility products have been avoided by using a levitation melting procedure to study chromium-oxygen interactions in liquid iron containing up to 24wt% chromium, under conditions which were sufficiently reducing to prevent the formation of chromium oxides at temperatures between 1550° and 1750°C. Kershaw *et al.*¹⁵ have used this technique to study oxygen activities in iron-vanadium alloys and have pointed out that with hydrogen/water-vapour mixtures to control the oxygen potential of the gas phase, thermal diffusion effects can lead to uncertainty in the gas composition at the droplet interface. For this reason their data were not used to calculate equilibrium constants. However by expressing the results in terms of an apparent equilibrium ratio, vanadium-oxygen interaction parameters were deter-

mined which were in good agreement with data from crucible experiments where thermal diffusion effects were eliminated by bubbling the gas through the melt. In the present work, further information has been obtained on the use of levitation melting to determine oxygen solution data for pure iron and iron-chromium alloys, by equilibrating droplets with H_2/H_2O and CO/CO_2 gas mixtures.

II. Experimental Procedure

A diagram of the levitation assembly is shown in Fig. 1. The experimental aspects of this procedure have been discussed in detail by Kershaw *et al.*¹⁵ In brief, power to the levitation coil was supplied from a 450 kHz, 10 kW generator, via a 7.5:1 step down transformer. The droplet was levitated inside a 15 mm vycor tube which was fitted with a rotatable aluminum base-plate containing a charging rod, a copper quenching mould and an observation port for temperature measurement by means of a two-colour pyrometer. Details on pyrometer calibration for use with a levitation system have been given previously.¹⁵ The temperatures reported are considered to be accurate to within $\pm 10^\circ C$. The oxygen potential of the atmosphere was controlled with either CO/CO_2 or H_2/H_2O

Fig. 1. The reaction chamber for levitation melting experiments

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gas mixtures. High purity CO/CO₂ mixtures were obtained with analysis from the supplier, while the H₂/H₂O mixtures were prepared by passing hydrogen over platinized asbestos and then through a water bath maintained within 0.1°C of the desired temperature in the range 30° to 47°C. Higher water vapour ratios were obtained by replacing the hydrogen with helium-hydrogen mixtures. In order to avoid oxide formation with the high chromium alloys, low water vapour ratios were produced by passing hydrogen over a mixture of oxalic acid and the acid dihydrate.¹⁶⁻¹⁹⁾ The behaviour of the saturator systems was checked with magnesium perchlorate bulbs and found to be within 0.5 to 1% of the expected values. Moisture condensation within the gas line from the saturator to the reaction chamber was prevented by means of a nichrome wire heater. Because of the difference in thermal properties, gas flow rates of approximately 20 and 0.5 l/min were required with CO/CO₂ and H₂/H₂O mixtures respectively, in order to maintain the droplet temperatures at the desired level.

In a typical experiment a one gram sample of Armco iron, or an iron-chromium alloy, was placed within the levitation chamber by means of the charging rod. After flushing with helium, the specimen was levitated, deoxidized in hydrogen for 5 min, and then exposed to either CO/CO₂ or H₂/H₂O for 5 to 10 min until steady state with respect to oxygen dissolution had been achieved. After quenching, samples were analysed for oxygen by inert gas fusion and for chromium by the standard oxidation procedure. Uncertainty in the oxygen analysis is less than 10 ppm, while the chromium values reported are accurate to within 2% of the amount present.

III. Discussion

1. Dissolution of Oxygen in Liquid Iron

Kershaw *et al.* have reported data for the dissolution of oxygen in levitated iron droplets exposed to hydrogen/water vapour gas mixtures.¹⁵⁾ Their data were significantly different from those obtained with conventional crucible techniques where precautions were taken to minimize error due to thermal diffusion.^{7,20,21)} The values of Kershaw *et al.* for the apparent equilibrium constant were unaffected by an eight fold change in gas flow rate. However when the mean molecular weight of the gas mixture was increased by the addition of argon, the values were in closer agreement with the data from crucible studies. These effects were attributed to the influence of thermal diffusion on the gas composition at the droplet interface and they have been confirmed in the present work.

Toop and Richardson have published data for the solution of oxygen in molten levitated nickel droplets which were equilibrated with CO/CO₂ gas mixtures.²²⁾ These gases are not as susceptible to thermal diffusion as H₂/H₂O and good agreement was observed between the levitation results and those from crucible experiments. During the course of the present study a series of experiments was made in which molten iron droplets were equilibrated with CO/CO₂ mixtures.

The reaction under consideration can be written:

for which: $K_1 = p_{\text{CO}_2}/p_{\text{CO}}[a_0]$, where K_1 is the equilibrium constant and a_0 is the oxygen activity based on the hypothetical 1 wt% solution. The equilibrium ratio for the reaction is:

$$K'_1 = p_{\text{CO}_2}/p_{\text{CO}}[\text{wt}\% \text{O}]$$

The variation of the equilibrium ratio with oxygen content was studied at 1600°C with gas mixtures ranging from 0.5 to 15%CO₂. The results are shown in Fig. 2. A least mean square treatment of the data showed that the deviation from Henry's law was not significant. This is in agreement with the findings of Tankins *et al.*²³⁾ The discrepancy caused by equating K_1 and K'_1 for the iron-oxygen binary, particularly for oxygen levels below 500 ppm, is considered to be well within the error limits of the oxygen analysis and is therefore ignored in further treatment of the data. The influence of temperature on K_1 was investigated from 1550° to 1750°C using a gas mixture containing 5.34%CO₂. The least mean square line corresponding to the present work in Fig. 3 has the equation:

$$\log K_1 = 7630/T(\pm 660) - 4.085(\pm 0.064) \dots\dots (1)$$

from which

Fig. 2. The effect of oxygen content on the equilibrium ratio at 1600°C for the reaction: $\text{CO} + \underline{\text{O}} = \text{CO}_2$

Fig. 3. Comparison of various data for the effect of temperature on the equilibrium constant for the reaction: $\text{CO} + \underline{\text{O}} = \text{CO}_2$

$$\Delta G_1^\circ = -34\,910 + 18.69\,T \dots\dots\dots(2)$$

For comparison purposes, results obtained by several other workers²⁴⁻²⁸⁾ who have studied this reaction using the crucible technique are included in Fig. 3. The solution of oxygen in liquid iron has been investigated most frequently with H₂/H₂O mixtures and for comparison with data from these studies, particularly levitation work, it is convenient to combine Eq. (2) with the free energy change for the water gas reaction:²⁹⁾

Thus for the reaction:

and

$$\log K_2 = 6\,242/T - 2.72 \dots\dots\dots(5)$$

The effect of temperature on log *K*₂ as represented by Eq. (5) is shown in Fig. 4 together with other correlations from the literature for this reaction.^{7,20,21,23,30,31)} Included in this figure, is a line representing the results from over sixty experiments performed during the present investigation in which levitated droplets were equilibrated with H₂/H₂O mixtures. These results are within 0.04 logarithmic units of the previous data from the levitation work by Kershaw *et al.*¹⁵⁾ It is evident from these findings that thermal diffusion effects are substantial when H₂/H₂O mixtures are used to control the oxygen potential of the system for levitation experiments of the type described here and for this reason the data should not be used directly to evaluate equilibrium constants. However it should be noted, that Sunderland *et al.*³²⁾ have combined the results of the present work with certain terms which were determined from consideration of thermal diffusion criteria and the kinetic theory of gases. The values which were then obtained for the equilibrium

constant were in very good agreement with previous data for this reaction.^{21,23,31)}

As would be expected from consideration of the molecular weight ratios, thermal diffusion effects are markedly decreased when CO/CO₂ mixtures are employed. In this case, the data for temperatures in the vicinity of 1 550° to 1 600°C are within 0.05 logarithmic units of the values from several previous studies, where conditions were adjusted to minimize errors from this source.^{7,20,21)}

2. Chromium-Oxygen Interactions in Liquid Iron

The major objective of the present study was to provide further evidence that the relative effect of one alloying element on the chemical behaviour of another, as represented by interaction parameters, could be determined by the levitation procedure, in spite of thermal diffusion, provided the gas composition at the droplet interface was not affected by the alloy content of the droplet. Experiments were performed at 50°C intervals between 1 550° and 1 750°C with alloys containing up to 24wt% chromium.

The equilibrium constant for the reaction between oxygen dissolved in liquid iron-chromium alloys and H₂-H₂O gas mixtures is given by:

$$K_2 = p_{\text{H}_2\text{O}}/p_{\text{H}_2} \cdot f_{\text{O}} \cdot [\text{wt}\% \text{O}] \dots\dots\dots(6)$$

where the reference state for the activity coefficient is based on the infinitely dilute solution.

From Eq. (6),

$$\log f_{\text{O}} = \log (p_{\text{H}_2\text{O}}/p_{\text{H}_2} [\% \text{O}]) - \log K_2. \dots\dots\dots(7)$$

Log *f*₀ can also be represented by a Taylor series expansion:

$$\begin{aligned} \log f_{\text{O}} &= e_{\text{O}}^{\text{O}} [\% \text{O}] + e_{\text{O}}^{\text{Cr}} [\% \text{Cr}] + r_{\text{O}}^{\text{O}} [\% \text{O}]^2 \\ &+ r_{\text{O}}^{\text{Cr}} [\% \text{Cr}]^2 + r_{\text{O}}^{\text{O,Cr}} [\% \text{O}] [\% \text{Cr}] + \dots \dots\dots(8) \end{aligned}$$

where the interaction parameters *e*₀^O, *e*₀^{Cr}, *etc.* are defined according to the formalism proposed by Wagner³³⁾ and subsequently developed by Lupis and Elliott.³⁴⁻³⁶⁾ In the present work, the oxygen level is sufficiently low so that terms involving *e*₀^O and *r*₀^O can be neglected. The parameter *r*₀^{O,Cr}, cannot be determined directly from the data available, however the term involving this parameter is likely to be small in comparison to the other second order term involving the square of the chromium content. This seems reasonable in view of the following empirical relationship³⁶⁾ between second order free energy parameters on a mole fraction scale:

$$\rho_i^{i,j} = \rho_i^i + \rho_i^j$$

With these considerations in mind Eq. (8) becomes:

$$\log f_{\text{O}} = e_{\text{O}}^{\text{Cr}} [\% \text{Cr}] + r_{\text{O}}^{\text{Cr}} [\% \text{Cr}]^2 \dots\dots\dots(9)$$

Combining Eqs. (7) and (9):

$$\begin{aligned} \log (p_{\text{H}_2\text{O}}/p_{\text{H}_2} [\% \text{O}]) &= e_{\text{O}}^{\text{Cr}} [\% \text{Cr}] \\ &+ r_{\text{O}}^{\text{Cr}} [\% \text{Cr}]^2 + \log K_2 \dots\dots\dots(10) \end{aligned}$$

Fig. 4. Comparison of various data for the effect of temperature on the equilibrium constant for the reaction: H₂ + O = H₂O

Results obtained from experiments conducted at 1 600°C are given in Table 1, while data for the effect of chromium on the equilibrium ratio are shown in Fig. 5. Values for first and second order free energy parameters were calculated from a least mean square analysis of the data collected at each temperature. The decrease observed in these parameters with increasing temperature is given by :

$$e_0^{Cr} = -557.8/T + 0.240 \dots\dots\dots(11)$$

and

$$r_0^{Cr} = 12.97/T - 6.29 \times 10^{-3} \dots\dots\dots(12)$$

From these relationships, the following values are calculated for first and second order enthalpy and entropy parameters on a wt% basis :

	Enthalpy	Entropy
First order	$h_0^{Cr} = -2\,550$	$s_0^{Cr} = -1.10$
Second order	$l_0^{Cr} = 59.34$	$p_0^{Cr} = 2.88 \times 10^{-2}$

The ratio of the first order enthalpy and entropy parameters on a mole fraction basis, $\gamma_0^{Cr} = -238$ kcal and $\sigma_0^{Cr} = -103$ cal/°K respectively, yields a value of 2 300°K for the “characteristic temperature” for iron-chromium-oxygen solutions. This represents the temperature at which the solution would become ideal, if the data at lower temperatures were linearly extra-

polated.³⁷⁾ Combining Eqs. (9), (11), and (12), the activity coefficient of oxygen in liquid iron-chromium alloys is given by :

$$\log f_o = (-557.8/T + 0.240)[\%Cr] + (12.97/T - 6.29 \times 10^{-3})[\%Cr]^2 \dots\dots(13)$$

which is valid for chromium concentrations up to 24wt% and for temperatures between 1 550° and 1 750°C. The influence of chromium concentration and temperature on the activity coefficient of oxygen is shown graphically in Fig. 6.

Experiments were also performed at 1 600°C with CO/CO₂ gas mixtures and iron alloys containing up to 10wt% chromium. It was determined by calculation, and subsequently confirmed by chemical analysis, that the effect of carbon dissolution from the gas phase on the behaviour of oxygen in the droplets, could be neglected. Treatment of the data was similar to that outlined previously and yielded the following equation for the activity coefficient of oxygen :

$$\log f_o = -0.058[\%Cr] + 1.25 \times 10^{-3}[\%Cr]^2 \dots\dots(14)$$

The value for e_0^{Cr} of -0.058 agrees well with that derived from Eq. (11) which was based on the H₂/H₂O experiments. The second order parameters are approximately 10⁻³ and agree within a factor of two.

Table 1. Dissolution of oxygen in iron-chromium alloys at 1 600°C from H₂/H₂O gas mixtures

Experiment number	Chromium (wt%)	(p_{H_2O}/p_{H_2}) ($\times 10^2$)	Oxygen (ppm)	$\log \frac{p_{H_2O}}{p_{H_2}[\%O]}$
1 331	0.52	5.539	121	0.661
1 333	0.52	5.529	118	0.671
1 334	0.52	5.529	116	0.678
1 335	0.52	5.529	127	0.639
1 321	1.01	5.580	99	0.751
1 322	1.01	5.584	110	0.706
1 323	1.01	5.584	113	0.694
1 324	1.01	5.623	114	0.693
1 325	1.01	5.623	113	0.697
1 350	1.95	5.478	160	0.535
1 351	1.95	5.478	165	0.521
1 353	1.95	5.482	161	0.532
1 461	7.67	1.988	92	0.335
1 462	7.67	1.988	67	0.472
1 463	7.67	1.988	80	0.395
1 464	9.99	1.987	102	0.290
1 465	9.99	1.987	125	0.201
1 466	9.99	1.986	116	0.234
1 467	15.00	1.985	195	0.008
1 468	15.00	1.981	179	0.044
1 469	15.00	1.984	186	0.028
1 470	19.99	1.985	281	-0.151
1 471	19.99	1.985	280	-0.149
1 472	19.99	1.987	282	-0.152
1 518	24.00	0.844	156	-0.267
1 519	24.00	0.844	157	-0.270
1 520	24.00	0.844	156	-0.267

Fig. 5. The effect of chromium on the equilibrium ratio for the reaction: H₂ + O = H₂O

Fig. 6. The effect of chromium on the activity coefficient of oxygen in liquid iron

This is not unreasonable in view of the fact that the chromium concentration did not exceed 10wt% in the CO/CO₂ experiments and for this reason the uncertainty associated with the second order parameter is somewhat greater than that associated with the first.

Goto *et al.*³⁸⁾ have measured the effect of chromium on the activity coefficient of oxygen in liquid iron at 1 560°C using CO/CO₂ gas mixtures. Although they did not report a value for the interaction parameter e_0^{Cr} , $\log f_0^{Cr}$ appeared to pass through a minimum point at about 7wt% chromium. The reason for this behaviour, which is quite different from that observed during all other investigations, including the present work, is still unclear.

Various values for the first order free energy interaction parameter, e_0^{Cr} , determined by different techniques are collected together in Table 2 and Fig. 7. Most of the determinations, including all of the EMF measurements, have been made in the vicinity of 1 600°C.

Three separate determinations have been made using lime-stabilized zirconia cells.¹²⁻¹⁴⁾ While all three values are in reasonable agreement, they correspond to the lowest values yet reported for the parameter. In contrast to the present work where $e_0^{Cr} = -0.058$, the average value from the EMF measurements is -0.034 . A similar situation is found when the various data for vanadium-oxygen interactions are compared.^{12,15)} If cell characteristics are such that the measured EMF yields values which, although internally consistent, differ significantly from the true oxygen activity, then subsequent calculation will produce values which should be considered not as interaction parameters and activity coefficients in

the accepted sense of the terms, but rather as “cell parameters” and “cell coefficients”. These cell terms would be dependent not only on the alloy content of the steel, but also the composition and properties of the electrolyte. Thus when electrochemical cells are used to determine dissolved oxygen contents in practical steelmaking operations, misleading results could be obtained if cell readings are combined with interaction parameter data derived by techniques other than those involving the use of a similar cell. Further work is required in order to clarify the reasons for these discrepancies. From previous investigations in which data were collected over a temperature range, two expressions have been reported for the temperature

Fig. 7. Comparison of various data for the free energy interaction parameter, e_0^{Cr} . The solid line corresponds to Eq. (11) from the present work and is based on H₂O/H₂ experiments with levitated droplets. Reference numbers are in parentheses.

Table 2. Chromium-oxygen interactions in liquid iron

	Chromium range (wt%)	Temperature (°C)	$-e_0^{Cr}$ (1 600°C)	Reference source
Water vapour/Hydrogen experiments	0-10	1 595	0.041	Chen and Chipman ¹⁾ ; Chipman ²⁾
	0-12	1 565-1 660 ^{a)}	0.064	Turkdogan ³⁾
	0-30	1 600	0.045 ^{b)}	Sakao and Sano ⁴⁾
	0-40	1 600-1 700	0.058	Charlton and Ahmad ⁵⁾
	0-10	1 723	0.058 ^{c)}	McLean and Bell ⁶⁾
	0-12	1 550-1 650 ^{a)}	0.037	Matoba and Kuwana ⁷⁾
	0-7	1 600	0.040	Schenck and Steinmetz ⁸⁾
	0-8	1 600	0.052	Pargeter ⁹⁾
Slag/Metal/Inert gas experiments	0-14	1 600-1 700	0.060	Kojima and Sano ¹⁰⁾
	10-25	1 600-1 800	0.047	Nakamura, Ohno, and Segawa ¹¹⁾
Electrochemical cell measurements	0-18	1 600	0.031	Fischer and Haussmann ¹²⁾
	0-51	1 600	0.037 ^{d)}	Fruehan ¹³⁾
	0-18	1 600	0.035	Cerkasov and Fischer ¹⁴⁾
Levitated droplets and H ₂ O/H ₂	0-24	1 550-1 750	0.058	This study
Levitated droplets and CO ₂ /CO	0-10	1 600	0.058	This study

a) The effect of temperature was not detectable.
b) For chromium concentrations below 10wt%.
c) Calculated assuming regular solution behaviour.
d) For chromium concentrations below 20wt%.

dependence of e_0^{Cr} , viz:

Kojima and Sano,¹⁰⁾

$$e_0^{Cr} = -369/T + 0.137 \dots\dots\dots(15)$$

and Nakamura *et al.*,¹¹⁾

$$e_0^{Cr} = -158/T + 0.038. \dots\dots\dots(16)$$

In the study by Kojima and Sano, iron–chromium melts were equilibrated with silica saturated slags and calculation of the above equation required the assumption that the available data on the temperature dependence for the effect of silicon on the behaviour of oxygen in liquid iron were not only correct but also applicable to iron alloys containing chromium. Previous work on silicon–oxygen interactions⁶⁾ and a recent study on the effect of chromium on the behaviour of oxygen in liquid iron–chromium–vanadium alloys, suggest this may not be so.¹⁴⁾ Nevertheless, the agreement between the present investigation and the work of Kojima and Sano is good, particularly at 1 600°C. Since there is evidence¹⁴⁾ that parameters determined for ternary solutions may not be applicable to multi-component melts, the value reported by McLean and Bell for e_0^{Cr} at 1 723°C may be too large.⁶⁾ This parameter was calculated from oxygen data for iron–chromium–aluminum melts and required the use of an aluminum–oxygen parameter evaluated from ternary solution data.

While the results from this study agree well with those of Nakamura *et al.* at 1 700°C, the variation of e_0^{Cr} with temperature is greater. In their case,¹¹⁾ no experiments were made with alloys containing less than 10wt% chromium and only first order parameters were employed to express the effect of chromium on the activity coefficient of oxygen. In the absence of measurements in the dilute solution range, the magnitude of the interaction parameter was based on the behaviour of the more concentrated solutions assuming a linear extrapolation to infinite dilution. In view of the curvilinear relationships shown in Fig. 6, this would imply that chromium–oxygen interactions have been underestimated, particularly at 1 600°C, where the second order effect is most pronounced. As the temperature increases, the system becomes more Henrian in behaviour and the extent of this error would diminish. This would account for the smaller temperature dependence represented by Eq. (16).

Continuing the investigation begun by Charlton,⁵⁾ Ahmad⁵⁾ reported a value for e_0^{Cr} of -0.044 at 1 700°C. This is in very good agreement with the value derived from the droplet experiments and when taken together with Charlton's value of -0.058 at 1 600°C, corresponds to a temperature dependence for the interaction parameter which is almost identical to that represented by Eq. (11). Although a temperature dependence was not reported, the data of Turkdogan³⁾ are in good agreement with the present study at 1 565°C.

Recently Dondelinger *et al.*³⁹⁾ have reported data for chromium–sulphur interactions in liquid iron which were determined by exposing levitated alloy droplets to H_2/H_2S mixtures. These gases are even more

susceptible to thermal diffusion than H_2/H_2O , nevertheless, the parameters were in excellent agreement with those obtained by Ban-ya and Chipman⁴⁰⁾ using a multiple crucible technique. The compatibility of the various data provides further confirmation that the levitation procedure can be employed to determine relative interactions in molten alloys, provided the gas composition at the droplet surface is not affected by the alloy content of the metal. This proviso also applies, of course, when gas/metal equilibria are investigated using crucible procedures. For example, it has been shown⁶⁾ that published data^{41–43)} for silicon interactions in liquid iron exposed to H_2/H_2O mixtures, contain discrepancies which can be attributed to alterations in the oxygen potential of the gas phase due to the formation of silicon monoxide.

IV. Summary

A study has been made of the dissolution of oxygen in liquid iron and iron–chromium alloys by equilibrating levitated droplets with H_2/H_2O and CO/CO_2 gas mixtures. Because of the presence of thermal diffusion, data from experiments of this type should not be employed to calculate equilibrium constants directly. Nevertheless, it has been proven that the levitation technique can be utilized to determine the relative effect of one alloying element on the chemical behaviour of another. During the present work it has been established that the effect of chromium on the activity coefficient of oxygen in liquid iron is given by:

$$\log f_o = (-557.8/T + 0.240)[\%Cr] \\ + (12.97/T - 6.29 \times 10^{-3})[\%Cr]^2$$

This equation is based on data derived from equilibration of H_2/H_2O gas mixtures with iron alloys containing up to 24wt% chromium at temperatures between 1 550° and 1 750°C. Data from CO/CO_2 experiments at 1 600°C with iron droplets containing up to 10wt% chromium are in good agreement with this expression.

While the value for e_0^{Cr} of -0.058 at 1 600°C is consistent with several previous studies based both on gas/metal and slag/metal, crucible experiments, it indicates a much stronger chromium–oxygen interaction than that suggested by recent electrochemical measurements with lime-stabilized zirconia cells. Further work is required in order to clarify the reasons for this discrepancy.

Advantages of the levitation procedure include: elimination of melt contamination by refractories, rapid attainment of equilibrium, and avoidance of analytical errors caused by solute segregation within samples.

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