

Slag-metal equilibrium in the smelting of high-carbon ferrochromium

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Synopsis

The equilibrium between carbon-saturated Fe-Cr-Si-C alloys and $\text{SiO}_2\text{-CaO-MgO-Al}_2\text{O}_3\text{-CrO}_x\text{-FeO}_y$ slags was studied under atmospheres of argon and carbon monoxide at temperatures of 1500 and 1600°C. The equilibrium distribution of chromium, silicon, and iron between the slag and the metal phases was determined for different compositions of both phases under different atmospheres and temperatures.

It is shown that silicon transfer from the slag to the metal increases with increasing temperature, decreasing carbon monoxide partial pressure, decreasing carbon content of the metal, increasing chromium-to-iron ratio of the metal, increasing silica content of the slag, and decreasing lime-to-alumina ratio of the slag. Some activity calculations were made for the experiments conducted at 1600°C in a carbon monoxide atmosphere.

It is also shown that a decrease in the iron content and an increase in the slag basicity decrease the chromium content of the slag. A major proportion of the chromium present in the slag was found to be in the divalent state under the highly reducing conditions prevailing in the experiments. The chromous capacities of these slags were calculated and were found to decrease with increasing basicity.

Samevatting

Die ewewig tussen koolstofversadigde Fe-Cr-Si-C legerings en $\text{SiO}_2\text{-CaO-MgO-Al}_2\text{O}_3\text{-CrO}_x\text{-FeO}_y$ -slakke is in argon- en koolstofmonoksiedatmosfeer by 1500 en 1600°C bestudeer. Die ewewigsverdeling van chroom, silikon en yster tussen die slak- en die metaalfase is vir verskillende samestellings van albei fases in verskillende atmosfere en temperature bepaal.

Daar word getoon dat die silikonoordrag van die slak na die metaal toeneem met stygende temperatuur, dalende koolstofmonoksiededruk, dalende koolstofinhoud van metaal, stygende chroom-yster verhouding van die metaal, stygende silikoinhoud van die slak, en 'n dalende kalk-aluminaverhouding van die slak. Daar is aktiwiteitsberekenings gedoen vir die eksperimente wat by 1600°C in 'n koolstofmonoksiedatmosfeer uitgevoer is.

Daar word ook getoon dat 'n vermindering van die ysterinhoud en 'n toename in die slak se basisiteit die chroominhoud van die slak verlaag. Daar is gevind dat 'n groot deel van die chroom wat in die slak aanwesig is, in die divalente toestand is in die uitsers reduserende toestande wat tydens die eksperimente heers. Die chroom kapasiteit van hierdie slakke is bereken en daar is gevind dat dit afneem met 'n toenemende basisiteit.

INTRODUCTION

Chromium is a commodity of critical and strategic importance, imparting unique qualities to the material to which it has been added. Most of the chromium used in the metallurgical industry is in the form of ferrochromium, which is available in either low-carbon or high-carbon forms. Owing to the development of steelmaking techniques involving oxygen-argon injection to a liquid-steel bath, permitting decarburization without significant loss of chromium, the use of high-carbon ferrochromium has increased tremendously. High-carbon ferrochromium is produced by the smelting of chromium ore in a submerged-arc furnace with a carbonaceous reducing agent in excess of that required to reduce the chromium and iron. The non-reducible oxides in the ore form slag and, although a self-fluxing charge is sometimes possible, fluxes must usually be added to produce a slag with the desired characteristics.

The study of slag-metal equilibria and reactions has always attracted the attention of researchers desirous of understanding the nature of the reactions and equilibrium conditions. Kinetic studies¹⁻³ pertinent to the present

system show general agreement that the reduction of chromium oxide from slags is a first-order reaction with respect to chromium, and the reaction rate is relatively independent of temperature and basicity in the range studied. The rate is limited by the transport of chromium from the bulk slag to the slag-metal interface. In the study of Maeda *et al.*³, the reduction of chromium from industrial slags into carbon-saturated iron was found to occur within 20 to 60 minutes, with a recovery of 90 to 99 per cent.

Several studies⁴⁻¹³ have been conducted on the phase equilibria, thermodynamics, and slag-metal equilibrium distribution of elements with fewer components than those of the present system⁴⁻¹².

It has been found that the equilibrium between the slag and metal phases at a given temperature is controlled by the compositions of the gas phase and the metal and slag phases.

In the Fe-Cr-Si-C metallic phase, it has been shown⁴ that an increase in chromium content causes an increase in the solubility of the carbon, but this effect can be neutralized by a simultaneous increase in the silicon content. An investigation⁵ of the phase equilibria in that system showed that the liquidus temperatures of the alloys increased with an increase in both the carbon and the ratio of chromium to iron. The primary phase during solidification was $(\text{Cr,Fe})_7\text{C}_3$ for the compositions studied, and its stability range expanded with an increase in the

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carbon content and the chromium-to-iron ratio, and with a decrease in the silicon content.

Muan⁶ studied the distribution of chromium between Fe-Cr-Si alloys and slags in the systems iron oxide-chromium oxide-SiO₂ and CaO-MgO-SiO₂-iron oxide-chromium oxide. He showed that the chromium in the slag phase was present predominantly in its divalent state, and concluded that increasing the basicity of the slag was an effective way of reducing the loss of chromium to the slag. In a similar study, Rankin and Biswas⁷ found that, in a slag under alumina saturation, 86 per cent of the chromium present in the slag was in its divalent state and, in slags under silica saturation, 92 per cent of the chromium in the slag was in its divalent state.

In their study of the thermodynamics of chromium oxide in CaO-MgO-Al₂O₃-SiO₂ slags in equilibrium with carbon, Maeda and Sano⁸ found that, at 1500 and 1650°C under an atmosphere of carbon monoxide, the slag was in equilibrium with Cr₃C₂ as well as with solid carbon. The chromium was found to exist as CrO in the slag, and the Cr²⁺ ion in the melt was found to behave amphotericly. In the CaO-Al₂O₃-SiO₂ melts, Al₂O₃ was observed to increase γ_{CrO} when chromium oxide behaved as a base. Thus, the equilibrium concentration of chromium in the melts decreased with increasing Al₂O₃ at constant CaO-to-SiO₂ ratios.

Rein and Chipman⁹ investigated the distribution of silicon between Fe-Si-C alloys and SiO₂-CaO-MgO-Al₂O₃ slags at 1600°C under an atmosphere of carbon monoxide. They also calculated the activities of SiO₂ in these slags¹⁰ by making use of the γ_{Si} values calculated by Chipman and Baschwitz¹¹. They showed that, as Al₂O₃ was substituted for CaO in slags of low SiO₂ content, the equilibrium silicon content of the metal increased⁹. In the case of slags with high SiO₂ contents, the opposite effect was observed. When SiO₂-CaO-MgO slags were in equilibrium with the metal phase, the silicon content of the metal remained approximately constant as MgO replaced CaO.

Despite these studies, there is very little fundamental information on SiO₂-CaO-MgO-Al₂O₃-CrO_x-FeO_y slags in equilibrium with Fe-Cr-Si-C alloys that is pertinent to the smelting of high-carbon ferrochromium. The present study was undertaken to obtain equilibrium data on the above-mentioned eight-component system mainly in terms of the silicon and chromium distributions between the metal and the slag phases.

EXPERIMENTAL PROCEDURE

The slags were prepared as homogeneous mixtures made from their analytical-grade pure components. These (consisting of Al₂O₃, CaO, SiO₂, and MgO) were calcined and homogenized for 24 hours at 1200°C in a muffle furnace prior to the experiments. Chromium oxide and iron oxide were added, when necessary, to these homogenized samples prior to experiments. The initial ranges of slag compositions were as follows:

SiO ₂	25-55%	MgO	3-30%,
CaO	3-35%	Al ₂ O ₃	25%.

The compositions were adjusted in such a way that the

basicity (*B*) of the slags varied from about 0,4 to 1,5. *B* was defined as (%CaO + %MgO)/%SiO₂.

The metal samples were master alloys that were prepared by the melting of pure reagent-grade iron, chromium, and silicon, and spectroscopic-grade graphite under vacuum. The appropriate alloy compositions were made by small additions of pure components to these master alloys as required. The composition ranges of the master alloys were as follows:

C	4-6%	Si	1-5%
Fe	30-43%	Cr	47-60%.

Samples of selected metal and slag in equal masses were placed in graphite crucibles and heated in a vertical molybdenum-wound resistance furnace. At the end of the equilibration, the crucibles were quenched by being dropped into water. The equilibration time was determined after a series of metal-slag equilibria runs, which were carried out at 1500°C at times varying from 3 to 14 hours but at the same initial compositions. The approach to equilibrium was established by analysis of the silicon content of the metal since the silica reduction is the slowest reaction in the present system¹². Both the oxidation and the reduction of silicon were investigated, although it is known¹² that silicon oxidation is four times faster than silica reduction at 1525°C. It was found by preliminary experiments that a minimum of 10 hours was necessary for equilibration at 1500°C. The approach to equilibrium in these experiments was established by determination of the silicon dissolved in the metal as a parameter. Both the reduction and the oxidation of silicon were investigated; reduction took 10 hours, oxidation being much quicker. The actual runs, however, were conducted for 12 hours.

Three series of experiments were undertaken, all under carbon saturation, namely at 1500°C under atmospheres of argon and carbon monoxide, and at 1600°C under carbon monoxide.

After equilibration and quenching, the distinct slag and metal phases were separated, cleaned when necessary, and sent for analysis. The carbon content of the metal was analysed by means of a Leco analyser, and the other constituents of the metal by the ICP method. The Al₂O₃, SiO₂, CaO, and MgO constituents of the slag were analysed by X-ray fluorescence, and its iron and chromium contents by the o-phenanthroline colorimetric and f-diphenylcarbazine colorimetric methods respectively. In addition, some X-ray-diffraction analyses and metallographic examinations were conducted on metal samples in order to detect the carbides.

RESULTS AND DISCUSSION

Over 150 experiments were conducted, from which 115 successful ones were selected for analysis. The failure of some experiments resulted from the loss of slag constituents due to the excessive evolution of gas. The problem was much more severe at 1600°C, when the argon atmosphere was used. At that temperature, almost all the slag overflowed from the crucibles, and the experiments at 1600°C under an argon atmosphere were consequently stopped. The slags from most tests were transparent and blue in colour, which was possibly an indication of the

existence of divalent chromium. The results are given in Tables I to III.

As expected from the studies of Wethmar⁵ and Griffing *et al.*¹⁴, the metallographic examination (employing potentiostatic etching) and X-ray analyses of the metallic samples revealed that all the metal phases from the experiments at 1500°C were saturated with respect to the (Cr, Fe)₇C₃ carbide. However, it was found that, at 1600°C, the equilibrium metal phases, with a few exceptions, were unsaturated with respect to the (Cr, Fe)₇C₃ carbide.

Distribution of Silicon

In the metal phase the carbon and silicon concentrations were inversely proportional. This well-known behaviour is illustrated in Figure 1 quantitatively for Fe-Cr-Si-C metallic solutions. The diagram shows that, as the chromium-to-iron ratio in the metal phase increased, the carbon solubility also increased and, at constant carbon contents, the silicon solubility in the metal increased with increasing chromium-to-iron ratio at both temperatures and under both atmospheres. When the results of the three

series of experiments are compared, it is seen that the lowest silicon levels in the metal phase were reached at 1500°C under an atmosphere of carbon monoxide.

The reason for this is the suppression of the silica reduction, reaction [1] under an atmosphere of pure carbon monoxide. The brackets in reaction [1] indicate the slag phase, and the bar under the species indicates the metallic phase. In equation [2], *K* is the equilibrium constant, *a_i* is the activity of species, and *P_i* is the partial pressure. The slopes of the curves in Figure 1 indicate that, at 1500°C under an argon atmosphere, the effect of the silicon concentration on the carbon concentration is more pronounced than it is under an atmosphere of carbon monoxide. As the temperature increased, the solubilities of both the carbon and the silicon in the metal phase also increased. This behaviour is consistent with the results of earlier investigations¹⁵.

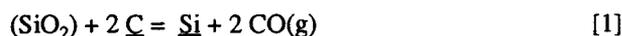


Table I
Results of slag-metal* equilibrium experiments at 1500°C under an argon atmosphere

Composition† of metal phase % by mass				Composition† of slag phase % by mass					
C	Cr	Si	Fe	SiO ₂	MgO	Al ₂ O ₃	CaO	Cr ₂ O ₃	Fe ₂ O ₃
7,53	46,64	3,57	42,45	43,87	21,97	27,69	5,98	0,370	0,257
7,41	47,20	3,43	41,80	35,66	9,73	26,67	27,74	0,100	0,100
7,83	47,32	3,25	41,60	41,69	3,61	24,52	29,84	0,183	0,153
7,56	47,01	4,14	41,28	52,66	14,33	25,37	7,11	0,349	0,184
7,16	47,34	4,36	41,13	52,43	11,49	25,31	10,17	0,390	0,203
8,38	47,47	3,12	41,02	37,79	7,99	25,81	27,99	0,183	0,234
7,76	47,56	3,77	40,91	40,62	4,78	26,51	27,82	0,149	0,113
7,55	51,85	4,15	36,34	48,16	2,77	25,85	21,81	0,870	0,542
7,28	52,40	4,12	36,69	46,94	23,47	27,24	1,31	0,488	0,280
7,20	52,06	4,29	36,43	47,13	23,78	27,34	1,24	0,303	0,146
7,16	52,29	4,15	36,38	43,48	16,55	25,51	13,96	0,308	0,185
7,87	52,14	3,74	36,24	44,94	22,61	26,56	5,49	0,257	0,123
7,48	52,70	3,42	36,36	43,62	9,67	24,99	19,86	1,231	0,625
7,20	52,51	4,10	36,19	48,96	20,99	27,12	2,29	0,336	0,305
7,33	52,85	3,47	36,35	39,99	4,12	24,66	30,98	0,123	0,113
7,18	52,50	4,43	36,00	54,21	4,04	25,18	16,17	0,239	0,104
7,12	52,60	4,70	35,57	50,29	21,19	25,70	2,17	0,413	0,237
7,17	52,98	4,06	35,79	45,04	3,30	26,12	25,10	0,241	0,185
7,12	52,92	4,31	35,65	46,50	10,30	26,19	16,56	0,266	0,184
7,70	53,60	4,80	33,29	55,00	5,98	24,88	13,60	0,425	0,132
7,97	54,76	3,68	33,59	43,29	10,20	25,59	20,50	0,236	0,174
8,05	55,17	3,37	33,40	40,58	4,26	24,79	29,96	0,272	0,136
8,07	55,02	4,15	32,77	48,78	4,94	24,77	19,62	1,228	0,653
8,47	55,08	3,66	32,78	43,79	3,89	24,95	26,28	0,500	0,189
7,65	55,21	4,33	32,80	46,64	23,97	27,46	1,26	0,472	0,189
7,98	55,05	4,52	32,45	47,50	15,31	25,36	11,10	0,473	0,247
8,49	55,53	3,42	32,47	42,08	3,74	23,51	29,63	0,378	0,174
7,85	55,70	4,03	32,31	52,55	3,08	25,37	18,58	0,272	0,141
7,94	55,77	4,68	31,61	53,92	10,43	26,05	9,02	0,425	0,152
7,81	55,96	4,56	31,66	53,48	14,53	25,56	5,25	0,863	0,315
8,17	59,94	2,77	29,12	44,94	9,14	25,58	19,88	0,297	0,164
8,28	60,65	2,69	28,38	54,16	13,69	24,64	6,91	0,439	0,153
8,59	60,64	2,89	27,87	54,09	10,23	25,96	9,07	0,391	0,257
8,88	61,61	2,34	27,17	38,01	7,15	24,77	23,94	0,730	0,394

* At equilibration temperature, all the metals were saturated with (Cr, Fe)₇C₃ carbide

† Normalized to 100

Table II
Results of slag-metal* equilibrium experiments at 1500°C under a CO atmosphere

Composition† of metal phase % by mass				Composition† of slag phase % by mass					
C	Cr	Si	Fe	SiO ₂	MgO	Al ₂ O ₃	CaO	Cr ₂ O ₃	Fe ₂ O ₃
7,80	47,02	2,39	43,90	43,85	17,94	24,91	12,90	0,292	0,100
7,76	46,81	2,52	42,90	43,44	13,54	24,84	16,94	0,301	0,151
7,43	47,00	3,11	42,44	51,00	13,32	23,80	11,75	0,453	0,122
7,51	47,16	3,06	42,27	49,60	22,68	23,84	3,37	0,718	0,329
7,74	47,39	2,39	42,47	44,25	4,08	25,52	25,82	0,239	0,090
7,43	47,17	3,20	42,15	49,85	3,96	24,30	20,69	0,307	0,089
7,36	47,46	3,02	42,16	50,11	9,65	24,27	15,48	0,396	0,089
7,38	46,50	2,68	41,30	46,38	14,57	25,32	13,27	0,351	0,114
7,86	47,54	2,48	42,11	43,95	8,72	25,36	21,52	0,262	0,191
7,42	47,62	3,01	41,95	48,08	18,51	24,77	7,92	0,481	0,180
7,91	47,65	2,46	41,97	43,55	22,52	25,02	8,46	0,331	0,107
7,99	48,03	1,77	42,22	39,43	8,46	25,21	26,57	0,206	0,113
7,96	48,09	1,92	42,03	39,66	3,78	25,31	30,96	0,192	0,091
8,05	48,18	1,70	42,07	39,87	13,32	25,25	21,29	0,149	0,090
7,99	50,03	2,13	39,84	38,91	14,04	24,85	21,38	0,506	0,314
7,55	51,19	3,01	38,25	49,73	13,52	24,45	11,86	0,353	0,091
7,55	51,31	3,03	38,10	50,27	9,80	24,15	15,19	0,292	0,159
7,81	51,63	2,46	38,10	44,74	4,09	25,36	25,50	0,212	0,081
7,66	51,37	3,12	37,83	49,41	22,74	24,05	3,32	0,379	0,100
7,44	51,71	2,76	38,08	43,32	18,17	25,18	12,88	0,303	0,142
8,17	51,90	1,72	38,20	39,76	3,99	25,03	30,90	0,205	0,100
7,55	51,52	3,02	37,91	50,08	17,88	23,95	7,59	0,407	0,102
7,53	50,70	2,66	37,30	45,97	12,08	24,83	16,25	0,571	0,306
7,64	51,79	2,52	38,05	44,33	8,83	25,25	21,26	0,247	0,082
8,32	51,78	1,99	37,92	38,83	8,79	24,68	26,18	0,581	0,400
7,71	51,61	2,89	37,79	50,53	3,96	24,41	20,62	0,362	0,105
7,77	51,84	2,60	37,78	43,90	13,53	25,06	17,13	0,285	0,102
7,90	51,89	2,49	37,71	43,53	22,59	24,73	8,45	0,351	0,181
7,66	56,34	3,50	32,49	48,68	23,02	24,28	3,52	0,403	0,091
7,62	56,35	3,58	32,44	49,12	18,08	24,43	7,84	0,394	0,131
7,67	56,89	2,75	32,69	43,42	8,79	25,06	21,26	0,923	0,351
7,74	56,57	3,14	32,44	49,02	9,97	24,68	15,59	0,493	0,249
7,65	56,40	3,20	32,34	49,68	3,94	24,12	20,74	1,011	0,496
7,73	56,74	2,85	32,51	42,92	22,86	25,10	8,67	0,349	0,090
8,07	56,88	2,52	32,53	44,32	4,18	24,96	25,67	0,438	0,149
7,70	57,09	3,12	32,09	49,75	13,42	24,45	11,96	0,321	0,090
7,95	57,28	2,75	32,02	42,59	17,60	24,56	14,61	1,590	1,079
7,88	57,63	2,54	31,99	43,42	13,53	25,11	17,50	0,348	0,092

* At equilibration temperature, all the metals were saturated with (Cr, Fe)₇C₃ carbide

† Normalized to 100

$$K_1 = \frac{a_{Si} P_{CO}^2}{a_{SiO_2} a_C} \quad [2]$$

The silicon content of the metal phase is directly proportional to the silica content of the slag with which it is in equilibrium. This is illustrated in Figure 2.

The increase of silicon content in the metal with increasing silica in the slag is more pronounced at 1600°C. This can be explained by the increase in the value of the equilibrium constant of reaction [1] as the temperature increases, shifting the reaction towards the right. For example, for a chromium-to-iron ratio of 1,7 in the metal phase (not illustrated in Figure 2), as the silica content of the slag increases from about 30 to 40 mass per cent, the silicon in the metal increases dramatically from 1,5 to 8,0 mass per cent.

The effect of the CaO-to-Al₂O₃ ratio on the silica

reduction is illustrated in Figure 3. In general, as the ratio increases, the silicon content of the metal decreases. This indicates that as, lime replaces alumina in the slag, the activity of silica in the slag decreases, in accordance with the network modification power of CaO; that is, the higher the content of CaO in the slag, the more will it break the silica network, releasing free oxygen ions and resulting in an increase in metal oxide activities and a decrease in silica activity. These present results are in agreement with those of Fulton and Chipman¹⁶. In another study⁹, as Al₂O₃ was replaced by lime in slags of low silica content, the equilibrium silicon content of the metal increased. In the case of high-silica slags (containing more than 20 per cent silica), the opposite effect was observed, which is in agreement with the present work, in that the silica contents of the present slags were above 26 per cent.

The effect of the MgO-to-CaO ratio on the partition ratio of silicon (% Si in slag / % Si in metal) is shown in Figure 4. It is observed that, as the ratio of MgO to CaO increases, the partition ratio decreases. This is an indication of the fact

Table III
Results of slag-metal equilibrium experiments at 1600°C under a CO atmosphere

Composition† of metal phase % by mass				Composition† of slag phase % by mass					
C	Cr	Si	Fe	SiO ₂	MgO	Al ₂ O ₃	CaO	Cr ₂ O ₃	Fe ₂ O ₃
6,26	44,96	8,17	40,61	37,28	16,02	30,74	15,54	0,222	0,182
4,90	43,81	11,71	39,57	26,50	31,27	36,12	5,64	0,267	0,203
7,27	46,27	4,88	41,57	38,57	4,21	28,08	28,84	0,193	0,091
7,92	46,88	3,21	42,00	36,20	3,94	27,09	32,36	0,197	0,207
6,33	45,63	7,18	40,86	37,01	21,71	30,28	10,37	0,325	0,203
6,45	45,54	7,35	40,66	38,14	11,19	30,39	19,88	0,263	0,132
7,99	46,89	3,30	41,81	35,75	14,56	26,75	22,56	0,238	0,129
7,18	46,07	5,74	41,02	38,94	9,29	27,81	23,65	0,204	0,102
7,85	46,85	4,19	41,71	36,05	8,85	26,88	27,88	0,209	0,119
7,08	46,30	5,40	41,22	39,50	24,15	26,97	8,99	0,281	0,099
6,77	45,90	6,68	40,64	39,63	16,06	28,22	15,70	0,261	0,118
6,87	46,28	6,26	40,59	39,46	18,83	27,06	14,21	0,351	0,090
7,54	49,81	4,70	39,63	36,55	20,35	27,22	14,84	0,656	0,375
7,04	49,01	5,91	38,05	38,06	9,82	27,61	24,01	0,330	0,175
6,46	47,83	8,61	37,09	39,70	21,84	29,65	10,18	0,429	0,194
7,88	49,75	3,99	38,38	39,08	14,60	27,12	18,73	0,328	0,144
7,33	49,05	5,80	37,81	38,84	15,61	29,44	15,19	0,570	0,352
*8,53	50,69	1,72	39,06	31,91	5,75	26,89	35,06	0,236	0,164
7,70	50,03	4,00	38,24	40,11	4,18	26,72	28,26	0,440	0,287
6,78	48,78	7,35	37,09	39,36	27,10	28,33	4,71	0,373	0,135
*8,58	50,96	1,87	38,58	32,13	2,88	26,66	37,89	0,266	0,163
7,13	49,08	6,79	37,04	41,36	10,80	27,04	17,79	0,396	0,180
8,04	50,71	3,46	37,79	36,62	14,83	25,97	22,30	0,198	0,083
7,72	50,46	4,25	37,57	34,76	8,80	26,87	28,93	0,330	0,222
8,31	50,64	3,12	37,53	32,68	4,37	27,83	34,66	0,266	0,187
7,52	49,80	4,59	36,70	35,83	19,42	27,48	16,80	0,288	0,170
*8,76	52,87	1,02	37,36	30,11	12,96	25,92	30,71	0,184	0,102
*8,86	54,89	0,83	35,41	30,10	7,19	24,99	37,45	0,155	0,103
*9,08	54,77	0,86	35,29	29,78	4,05	24,34	41,55	0,173	0,101
*8,58	54,43	1,68	35,00	32,96	13,30	26,13	27,25	0,270	0,102
*8,71	54,13	1,80	34,76	33,48	9,78	26,03	30,45	0,203	0,094
7,02	53,01	8,06	30,90	37,85	21,20	30,11	10,27	0,366	0,193
7,60	54,98	5,36	31,83	35,87	14,34	29,16	20,30	0,232	0,095
7,62	55,21	5,32	31,85	37,42	9,14	28,54	24,59	0,218	0,094
7,11	54,28	7,30	31,30	39,29	27,74	27,74	4,86	0,228	0,134
*8,23	55,62	4,02	31,94	32,91	8,57	27,93	30,18	0,274	0,142
7,19	53,94	8,01	30,85	37,63	16,24	30,30	15,41	0,277	0,143
*8,25	55,51	4,50	31,73	33,06	14,03	28,32	24,19	0,244	0,152
7,43	55,04	6,19	31,34	39,44	19,01	26,88	14,09	0,375	0,213
7,49	54,60	6,90	31,00	38,25	4,52	30,38	26,01	0,568	0,257
7,37	54,02	6,55	30,47	37,97	11,44	30,52	19,74	0,231	0,094
7,44	55,03	6,78	30,54	41,65	20,64	25,37	9,79	1,717	0,832
7,45	55,01	7,25	30,28	41,42	26,70	25,19	5,70	0,595	0,243

* At equilibration temperature, all these metals were saturated with (Cr, Fe)₇C₃ carbide

† Normalized to 100

that, as MgO replaces CaO in the slag, the activity of silica in the slag increases, resulting in an increase in the silicon content of the metal.

In Rein and Chipman's study¹⁰, the activities of silica (with respect to the solid cristobolite form of silica as the standard state) in the SiO₂-CaO-MgO-Al₂O₃ system were calculated at 1600°C and 1700°C by making use of the work of Chipman and Baschwitz¹¹, who found that γ_{Si} in the Fe-Si-C ternary solution is approximately the same function of $X_{Si} + X_C$ as it is of X_{Si} in the carbon-free binary system, where γ_{Si} is the activity coefficient of silicon and X_i are the mole fractions. It was possible to obtain silica activities from the iso-activity curves of their work at constant MgO and Al₂O₃ concentrations that are pertinent to some slag compositions in the present work. However, because of the difficulties involved in accurate reading of their data from the available diagrams, these silica activities

are considered to be only approximate. By use of the equilibrium constant for reaction [1], $K_1 = 0,2184$ and, since $a_c = 1,0$ and $P_{CO} = 1,0$ atm. in the present work at 1600°C, a_{Si} (with pure liquid silicon as the standard state) in some of the carbon saturated Fe-Cr-Si-C alloys was calculated. The results, shown in Table IV and Figure 5 within the dilute range studied, have considerable negative deviation.

Distribution of Chromium

In the present study, the chromium and iron contents of the slags were very low. The slags usually contained less than 0,5 per cent Cr₂O₃ and 0,3 per cent Fe₂O₃ by mass. Even when these two oxides were initially added up to 10 per cent to the charge in a number of experiments, they were reduced to their equilibrium values indicated above. This was mainly due to the highly reducing conditions

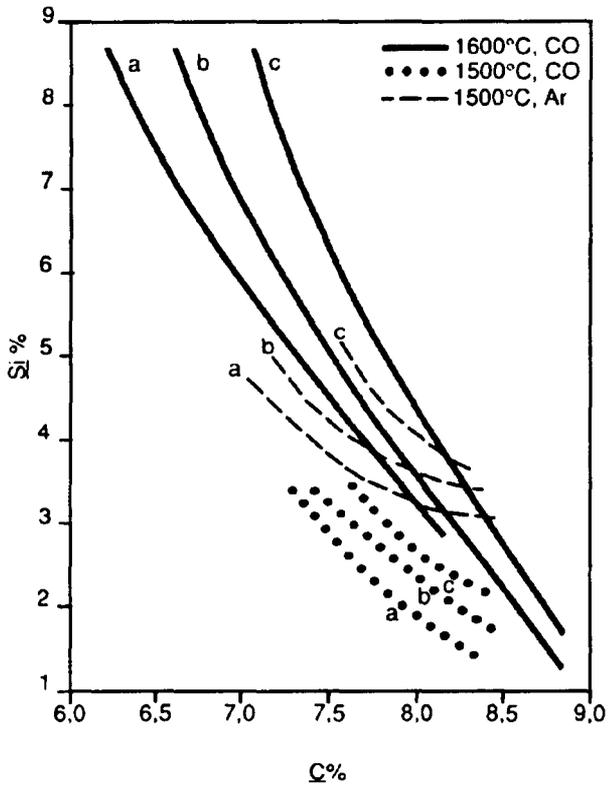


Figure 1—The effect of the silicon content on the carbon content of the metal. Approximate chromium-to-iron ratios (all for the metal phase): a 1,1; b 1,3; c 1,7

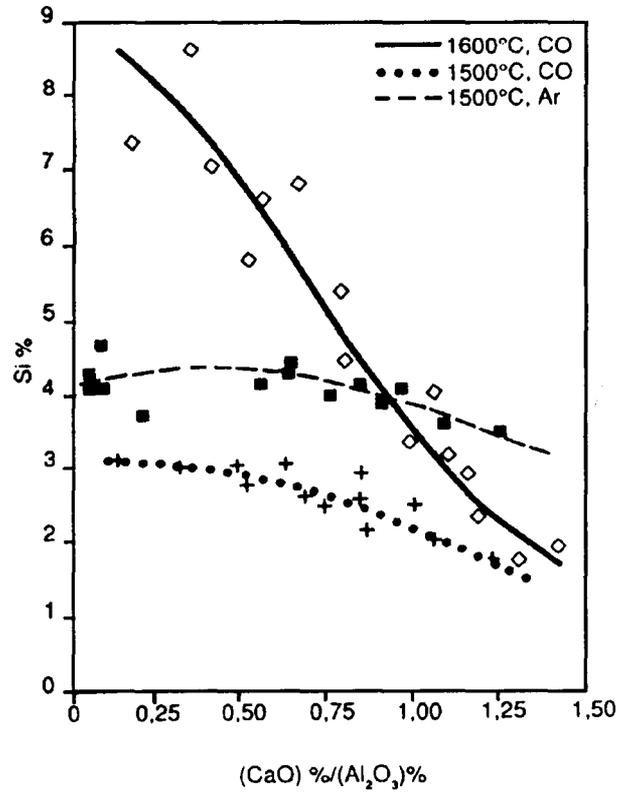


Figure 3—The effect of the lime-to-alumina ratio of the slag on the silicon content of the metal at a chromium-to-iron ratio of approximately 1,3 in the metal phase

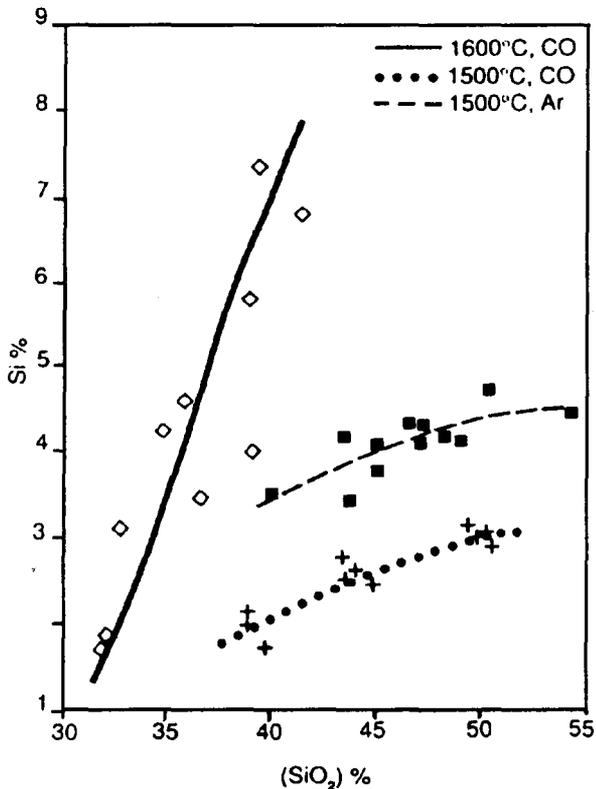


Figure 2—The effect of the silica content of the slag phase on the silicon content of the metal phase at a chromium-to-iron ratio of approximately 1,3 in the metal phase

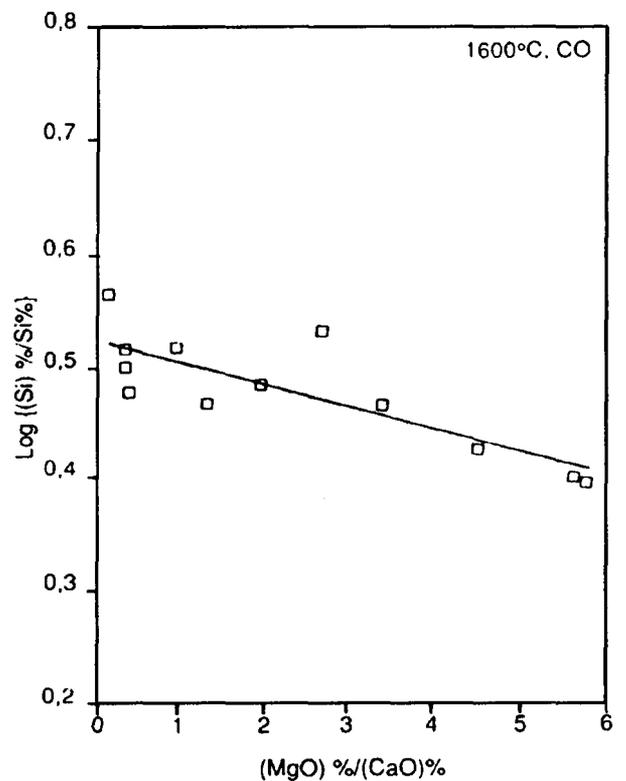


Figure 4—The effect of the MgO-to-CaO ratio on the silicon distribution at 25 per cent alumina and 39,3 per cent silica

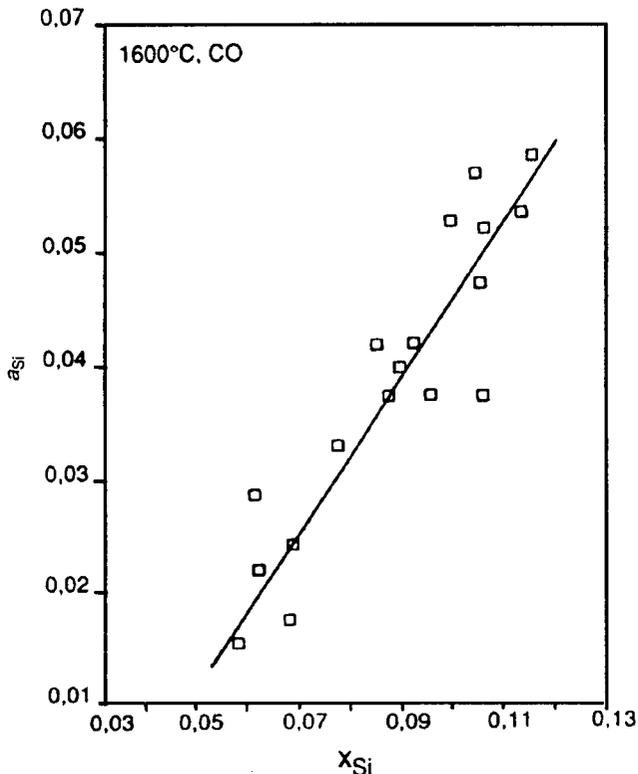


Figure 5—The change in a_{Si} with X_{Si} in Fe-Cr-Si-C (saturated) alloys

prevailing in the present experiments.

The effect of basicity on the chromium content of the slags is shown in Figure 6. At low basicities, the chromium content (calculated as Cr) of the slag decreased rapidly as the basicity increased from 0,4 to 0,8 at 1500°C for argon and carbon monoxide atmospheres and from 0,7 to 1,0 at 1600°C for carbon monoxide atmospheres. Thereafter, once the threshold value had been passed, the basicity did not dramatically affect the chromium solubility in the slag, which tended to a constant value around 0,15 per cent by mass. This behaviour proves that operation with high basic slags just above the threshold value is a means of lowering chemical chromium losses to the slag.

A slag-metal reaction can be written between the iron oxide and the chromium oxide components of the slag on the assumption⁶ that all the iron is present as FeO :



Since activity coefficients are not known, an 'apparent equilibrium constant' could be used employing the concentrations

$$K' = \frac{(\% \text{Fe})^x (\% \text{CrO}_x)}{(\% \text{FeO})^x (\% \text{Cr})} \quad [4]$$

If the partition ratios are defined as $L_{Fe} = (\% \text{ Fe in slag}) / (\% \text{ Fe in metal})$ and $L_{Cr} = (\% \text{ Cr in slag}) / (\% \text{ Cr in metal})$, equation [4] can be rearranged into

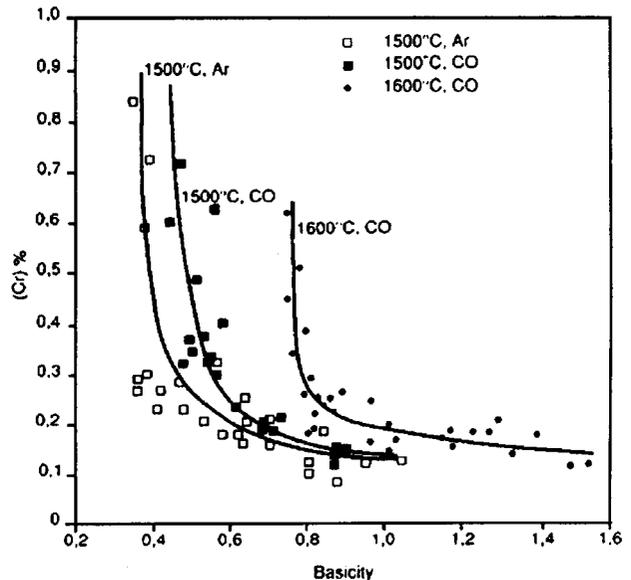


Figure 6—The effect of basicity on the chromium content of slags

$$\log L_{Cr} = x \log L_{Fe} + \log K' \quad [5]$$

Equation [5] is linear, with slope 'x' and intercept $\log K'$. These graphs were plotted for all three series of experiments. A typical plot is shown in Figure 7 for the data at 1500°C under an argon atmosphere. The slope is 0,86. In the other experimental series, the slope was also less than unity, being 0,73 for 1600°C and 0,62 for 1500°C, both under carbon monoxide. The slopes being close to unity indicate the presence of divalent chromium ions in the slag in significant amounts. A possible reason for the value of x being less than unity is the presence of metallic chromium in the slag. This may have resulted from the entrapment of metal, rather than from disproportionation of CrO in the slag. The dissociation can occur in slowly cooled slags:



If such a disproportionation had occurred, the metallic inclusions would have been associated with the Cr_2O_3 reaction product. This was not the case in the present work, since the samples were quenched very quickly from equilibrium temperature, and metallographic examination of the slag did not show such co-precipitation.

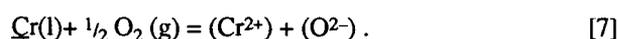
The effect of FeO in the slag on its chromium content is illustrated in Figure 8. This typical diagram is for experiments done at 1500°C under an argon atmosphere. There is direct proportionality between the chromium and the iron contents of the slag, in agreement with earlier rather qualitative results^{2,7}. Such behaviour can be explained by the phenomenon of oxygen transfer from the slag to the metal phase by means of FeO; that is, FeO in the slag oxidizes chromium in the metal phase at the slag-metal interface. Thus, the more FeO the slag contains, the more will be its chromium content.

Table IV

Slags in equilibrium with metal phases for which the activities of silicon in the metal were calculated from known activities of silica

Slag composition, %				Activity of SiO ₂ in the slag	Metal composition, %					Calculated activity of Si in the metal
SiO ₂	MgO	Al ₂ O ₃	CaO		Si	Fe	Cr	C	Mole fraction of Si in the metal phase	
32,91	8,57	27,93	30,18	0,07	4,02	31,94	55,62	8,23	0,0582	0,0154
34,76	8,80	26,87	28,93	0,10	4,25	37,57	50,46	7,72	0,0621	0,0220
36,05	8,85	26,88	27,88	0,13	4,19	41,71	46,85	7,85	0,0608	0,0286
37,42	9,14	28,54	24,59	0,15	5,32	31,85	55,21	7,62	0,0771	0,0330
38,06	9,82	27,61	24,01	0,17	5,91	38,05	49,01	7,04	0,0869	0,0374
38,14	11,19	30,39	19,88	0,17	7,35	40,66	45,54	6,45	0,1089	0,0374
38,94	9,29	27,81	23,65	0,19	5,74	41,02	46,07	7,18	0,0843	0,0418
41,36	10,80	27,04	17,79	0,24	6,79	37,04	49,08	7,13	0,0989	0,0528
35,83	19,42	27,48	16,80	0,08	4,59	36,70	49,80	7,52	0,0679	0,0176
36,55	20,35	27,22	14,84	0,11	4,70	39,63	49,81	7,54	0,0684	0,0242
37,01	21,71	30,28	10,37	0,12	7,18	40,86	45,63	6,33	0,1068	0,0264
39,46	18,83	27,06	14,21	0,19	6,26	40,59	46,28	6,87	0,0924	0,0418
39,44	19,01	26,88	14,09	0,18	6,19	31,34	55,04	7,43	0,0896	0,0396
39,70	21,84	29,65	10,18	0,19	8,61	37,09	47,83	6,46	0,1262	0,0429
41,65	20,64	25,37	9,79	0,25	6,78	30,54	55,03	7,44	0,0979	0,0561
39,29	27,74	27,74	4,86	0,17	7,30	31,30	54,28	7,11	0,1058	0,0374
39,36	27,10	28,33	4,71	0,17	7,35	37,09	48,78	6,78	0,1077	0,0374
41,42	26,70	25,19	5,70	0,26	7,25	30,28	55,01	7,45	0,1041	0,0572

The solubility of chromium in slags was also analysed in terms of the chromous capacity. The 'chromous capacity' can be interpreted according to the reaction



The equilibrium constant for reaction [7] will be

$$K = \frac{(a_{\text{O}^{2-}})(\gamma_{\text{Cr}^{2+}})(C_{\text{Cr}})}{P_{\text{O}_2}^{1/2} a_{\text{Cr}}} \quad [8]$$

The chromous capacity is then obtained from equation [8] as

$$C_{\text{Cr}^{2+}} = \frac{C_{\text{Cr}}}{P_{\text{O}_2}^{1/2} a_{\text{Cr}}} = \frac{K}{a_{\text{O}^{2-}} \gamma_{\text{Cr}^{2+}}}, \quad [9]$$

where $C_{\text{Cr}^{2+}}$ is the chromous capacity and C_{Cr} is the concentration of chromium (expressed in mole fractions) in the slag assumed to be in divalent state. P_{O_2} is the partial pressure of the oxygen in the gas phase, and the other terms have their usual meaning. The definition and use of 'capacity' stems from the fact that none of the terms in equation [9] on the far right-hand side can be defined or measured individually, but those to the right of the first equals sign can be measured and/or calculated. The capacity of the slag for a species is a function of the composition of the slag, the temperature, and the prevailing atmosphere. The concept of capacity is most appropriate to those species which have low solubility in slags for conditions prevailing in typical metallurgical operations, in particular for total pressures not much greater than

atmospheric. It has become fairly popular for use in the empirical correlation of solubility data, and will probably be extended to many species in the future. In this regard, the chromous capacity introduced here is unique and most probably the first of its kind to be used in this way.

The oxygen partial pressure in formula [9] is calculated from the following reaction on the assumption that the oxygen potential of the gas phase in the experiments is controlled by the carbon monoxide gas and the graphite crucible:



$$\Delta G^\circ = -111712,8 - 87,65 T \quad \text{J/mol} \quad [11]$$

For this reason, the calculations had to be confined to the experiments under carbon monoxide both at 1500°C and 1600°C where $P_{\text{CO}} = 1,0$ atm., as well as $a_{\text{C}} = 1,0$. In the absence of chromium activity data for carbon-saturated Fe-Cr-Si-C alloys, the a_{Cr} values were calculated by use of the method reported by Healy¹⁷ for the Fe-Cr-C system on the assumption that silicon was absent in the metal phase. However, as the silicon is the dilute component in most of the metal phases and chromium (together with iron) is the major solvent, the activity of chromium is not expected to be altered greatly by that of silicon. Nevertheless, the values of chromous capacity calculated here should not be treated as absolute values. The chromous capacities are plotted against basicity in Figures 9 and 10. As the basicity increases, the dissolving power of the slag with respect to Cr²⁺ ions decreases. This is further proof of the depolymerization of the melt with increasing basicity, resulting in an increase in the activity of oxygen ions. Also interesting to note are the higher chromous-capacity values at lower temperature. This is not unusual, since the reduction of chromium ions to metallic phase is

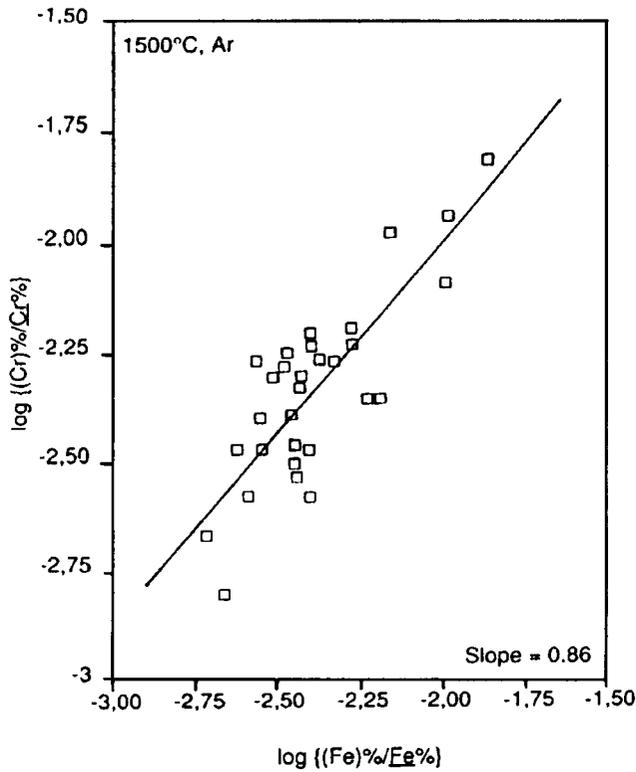


Figure 7—The variation in the log partition ratio of chromium with the log partition ratio of iron

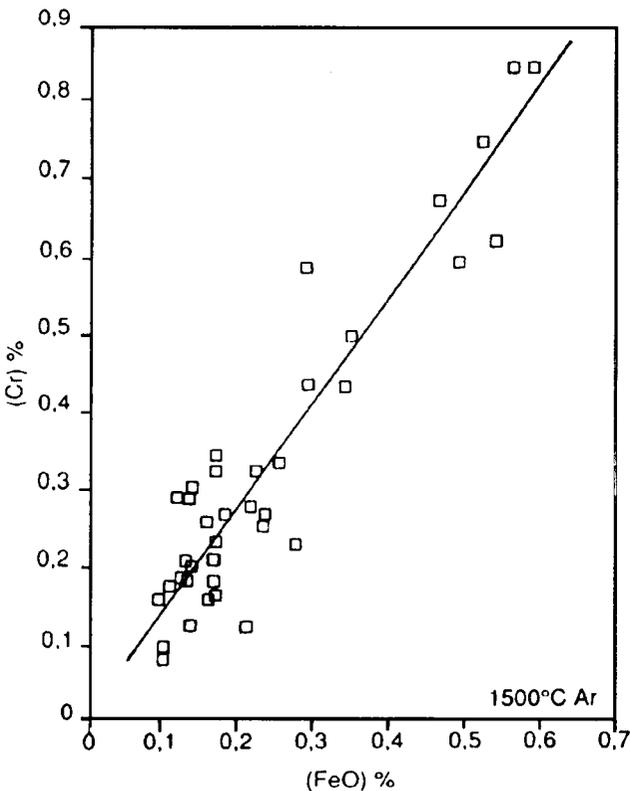


Figure 8—The effect of FeO on the chromium content of the slag

more favourable at higher temperatures.

SUMMARY AND CONCLUSIONS

The investigation reported here is possibly the first of its kind related to high-carbon ferrochromium smelting in that it deals with a complex slag-metal equilibrium involving eight components distributed between the Fe-Cr-C-Si metal phase and the SiO_2 -CaO-MgO- Al_2O_3 - CrO_x -FeO_y slag phase. The metal and slag compositions and temperatures studied are relevant to actual ferrochromium-smelting operations.

It was shown that, in the metal phase, the concentrations of carbon and silicon are inversely proportional to each other and that, as the chromium concentration and the temperature increase, the solubility of both the silicon and the carbon in the metal phases increases.

The silicon content of the metal phase increases as the silica content of the slag increases.

As the CaO-to- Al_2O_3 ratio of the slag increases, the silicon content of the metal phase decreases. This possibly indicates that, as lime replaces alumina in the slag, the activity of silica in the slag decreases.

As the MgO-to-CaO ratio of the slag increases, the silicon partition ratio (%Si in slag / %Si in metal) decreases slightly. This possibly indicates that, as MgO replaces CaO, the activity of silica in the slag increases.

It was also shown that the chromium content of the slag increases with increasing iron content of the slag, but decreases as the basicity increases, and that this second

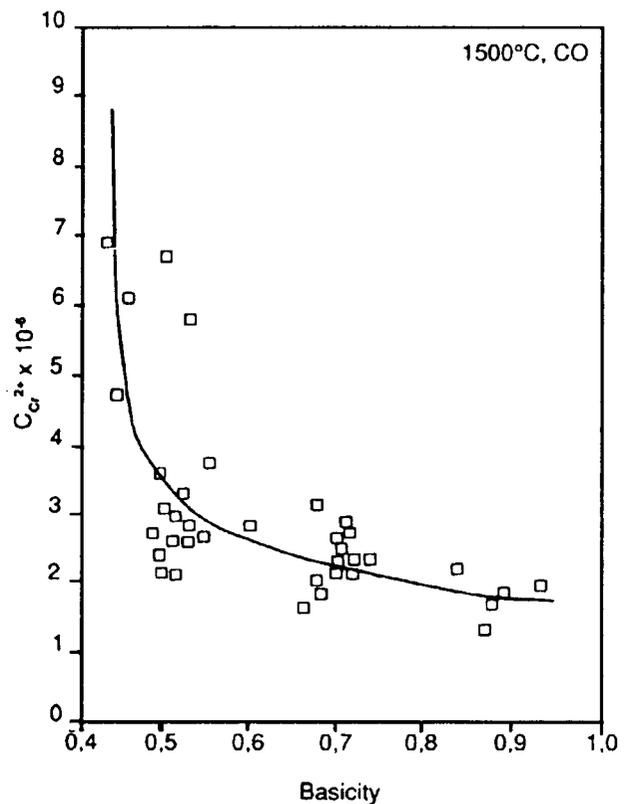


Figure 9—The effect of basicity on the chromous capacity of slags at 1500°C

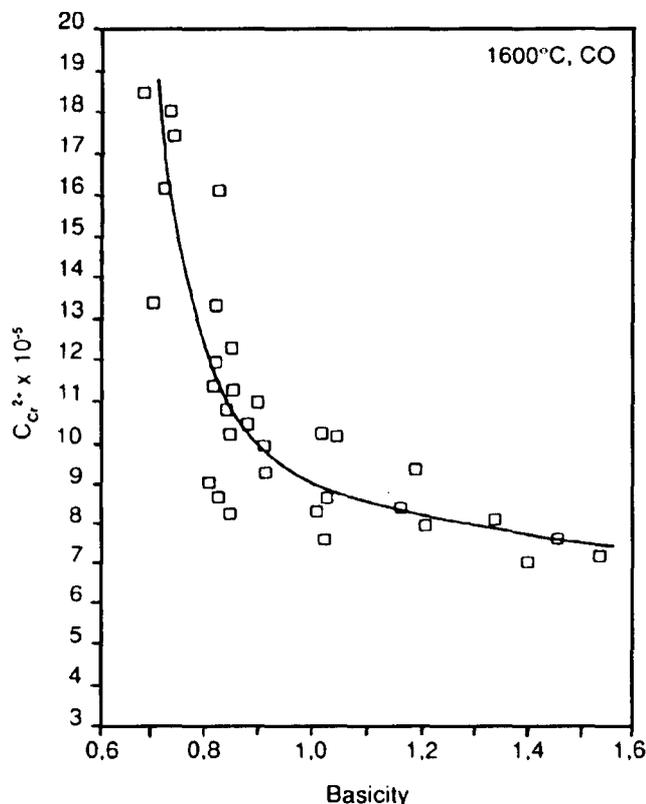


Figure 10—The effect of basicity on the chromous capacity of slags at 1600°C

effect is stronger at relatively low basicities. Chromium occurs in the slag phase mainly in divalent form at high temperatures, and the chromous capacity of slags pertinent to the production of ferrochromium decreases with increasing basicity and temperature.

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Mineral-engineering research at Wits

by R.H. Eric*

At the beginning of 1992, the Department of Metallurgy and Materials Engineering of the University of the Witwatersrand issued its 1990/91 research report, which covered the projects that were in progress from mid 1990 to mid 1991. The Department is, and has always been, very active in the research field, and has established a worldwide reputation in various fields. The research in the department falls into six main topics: coal, corrosion, fracture, materials processing, mineral processing and hydrometallurgy, and pyrometallurgy (in alphabetical order), as well as the development of computer software.

PROJECTS

In the three projects under coal studies, emphasis was placed on improved categorization, beneficiation, and usage of South African coals with their high mineral content.

The corrosion group worked on eight projects, the accent being on alloy development. However, there was a greater spread in the activities than ever before. Projects are under way, not only on stainless steels, but also on aluminium alloys. There is close collaboration with the CSIR on some of the projects.

On the topic of fracture, nine projects were conducted, the research involving a large spectrum of activities. Wear of ceramics, development of hard metals, predictions of fatigue life, and studies of fracture mechanics were part of the programme. The highlight of 1991 was a two-day seminar that was held in November on creep and creep fracture, which was sponsored by the Board of Acta Metallurgica Inc.

The activities in materials processing were aimed chiefly at the development of materials and processing methods in order to maximize the utilization of local resources, optimize processing methods, and thus enhance value addition to commodities through manufacturing. Nine projects were in progress involving, among others, the development of diffusion carbide coatings, the use of aluminium-ruthenium alloys, the modification of cast structures of stainless steels, and the effect of nitrogen on austenitic stainless steels.

Current research in minerals processing and hydrometallurgy covers a broad spectrum of activities. Significant progress has been made in the hydrometallurgy field. A new laboratory has been constructed involving a unique column type of reactor that can be operated to about 160 °C and 500 kPa. A flexible, well-controlled rig has also been built for the elution of metals from activated carbon or resins. In the mineral-processing area, activities are centred on the development of a quantitative understanding of various unit operations. The CIP process is still attracting significant effort. The highlight of the year was the award of the South African Institute of Mining and Metallurgy

Gold Medal for a series of papers written by members of the Department dealing with the modelling and simulation of the adsorption process. All in all, the fifteen projects conducted by this group were more or less evenly distributed between classical mineral processing and hydrometallurgy.

The pyrometallurgy group has close ties with Mintek and the ferro-alloy industry through the Ferro Alloy Producers' Association. Fundamental studies are undertaken to understand, quantify, and model existing and new unit processes in the production of ferro-alloys and stainless steel. Fundamental studies related to the processing of base and precious metals are also under way. Two new high-temperature furnaces capable of reaching 1800 °C by the use of lanthanum-chromite heating elements have been added to the laboratory, and a new state-of-the-art computerized thermogravimetric facility was built. Over the years, a wealth of information and knowledge has been gathered on these pyrometallurgical topics, and major break-throughs have been achieved in understanding the fundamentals of fluxed and unfluxed solid-state reduction and reduction in liquid alloys. Thirteen projects were undertaken by this group.

The development of computer software continues to form an interesting aspect of the overall departmental activities. An agreement with a local company, Kenwalt, is being reached by which Kenwalt will acquire the rights to the packages Microsim and MicBal. It is believed that this is the best way of continuing the development of the software and promoting its use in the industry. This should result in a more successful transfer of technology.

PUBLICATIONS

It is the policy of the Department of Metallurgy and Materials Engineering to publish and disseminate the results of its activities as widely as possible. Publications in international and local journals, and presentations at international conferences, are strongly encouraged, enabling the Department to disseminate information to a wide international audience. The Department has established a sound international reputation through its high-quality publications. It has produced fourteen international publications, including conference proceedings, and there are eleven more publications in the press within the terms summarized in the research report. A total of seventy-one departmental reports were prepared and published during this period.

CONTACT

The Department would like to encourage researchers in other universities and research organizations, as well as engineers in industry, to make contact with researchers in the Department, who will welcome the possibility of collaboration in solving their problems.

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