

Liquidus temperatures in the Cr-Fe-Si system in the composition range representative of ferrochromium-silicide produced in South Africa

J. C. M. Wethmar,* B.Sc. (Eng.) Rand
D. D. Howat,** B.Sc. (Glas.), Ph.D., F.I.M.
P. R. Jochens,* Pr.Eng., M.Sc. (Eng.) Rand, Ph.D., A.I.M.
O. A. W. Strydom,* M.Sc., Ph.D.

SYNOPSIS

Alloys in the composition range of chromium, 20 to 50 per cent, iron, 10 to 30 per cent, and silicon, 25 to 55 per cent, were subjected to both differential thermal analysis and the classical quench method so that the liquidus temperatures of ferrochromium-silicide alloys could be determined. The results are presented as liquidus curves on pseudo-binary sections at various ratios of chromium to iron and as liquidus isotherms in the ternary section.

SINOPSIS

Allooie met samestellings wat varieer vanaf 20 tot 50 persent chroom, 10 tot 30 persent yster, en 25 tot 55 persent silikon was onderwerp aan beide differensiële termiese analise en die klassieke blusmetode sodat die smeltpunt temperatuur van ferrochroom-silisiëde allooie bepaal kon word. Die resultate word as smeltpunktkromme weergegee op pseudo-binêre seksies van verskillende verhoudinge van chroom tot yster en ook as smeltpunt isoterme in die ternêre seksie.

INTRODUCTION

The alloy, ferrochromium-silicide may be produced either by the smelting of chromite ore, together with a reducing agent, silica, and fluxes ('slag process'), or by the smelting of high-carbon ferrochromium, together with a reducing agent and silica ('dry process'), in an electric smelting furnace. An important factor in the optimization of the smelting process that involves the production of slag is the relation between the liquidus temperature of the alloy and that of slag. Once the components of the charge have reached the smelting zone, and have reacted and fused, the products of reaction—alloy and slag—will drop away from the area of intense heat surrounding the electrode tips and will settle into the furnace hearth. Consequently, if the alloy is to be superheated to the required degree for pouring and casting, the liquidus temperature and viscosity of the slag must be such that the slag and

alloy can drain away from the arc zone only when the alloy has attained the desired degree of superheating. Conversely, if the alloy is tapped at an excessively high temperature, the consumption of electric power and the rate of refractory wear will increase. Hence, a knowledge of the liquidus temperatures of the ferrochromium-silicide alloys is essential for efficient operation. This knowledge is also required in an assessment of the optimum tapping temperature when the ferrochromium-silicide is produced from high-carbon ferrochromium without the production of slag.

It is common practice to let the ladle stand undisturbed for a considerable period so that the carbon-rich constituents can rise to the surface and the carbon content can thus be reduced to a minimum. Under these conditions it is essential to have precise information about the liquidus temperatures of the alloys. If the exothermic reaction between lime-chromite ore melt and ferrochromium-silicide is carried out to produce low-carbon ferrochrom-

ium with molten silicide, then it is essential that the reaction is commenced before the silicide starts to freeze in the ladle.

The binary phase relations in the system chromium-iron-silicon have been reported by Hansen¹. The ternary phase relations in the iron-chromium-silicon system have been investigated by Denecke², Anderson and Jetté^{3, 4}, Sveshnikov and Alferova⁵, Elyutin et al.⁶, Kurnakov^{7, 8}, Dubrovskaya and Gel'd⁹, Petrushevskii¹⁰, and Gladyshevskiy and Borusevich¹¹. Some phase constitution data for the chromium-iron-silicon system can also be derived from studies made by Lucas and Wentrup¹², Jetté and Anderson¹³, Kurnakov^{14, 15}, Caron¹⁶, Kadarmetov¹⁷, and Petrushevskii and Gel'd¹⁸ on the solubility of carbon in chromium-iron-silicon alloys. However, there is insufficient information for the plotting of liquidus isotherms for ferrochromium-silicide alloys representative of those produced in South Africa, i.e. within the composition range of chromium, 20 to 50 per cent, iron 10 to 30 per cent, and silicon, 25 to 55 per cent.

*N.I.M. Pyrometallurgical Research Group.
**Department of Metallurgy, University of the Witwatersrand.

EXPERIMENTAL

Synthetic alloys were premelted and subjected to differential thermal analysis. The results were confirmed by the classical quench method.

Sample Preparation

The compositions of twenty-six alloys were so selected that the ternary system was subdivided into five pseudo-binary sections at selected ratios of chromium to iron. Samples of 30 g mass were weighed out from the pure components and melted in alumina crucibles in a Degussa furnace with a carbon resistance element under a protective atmosphere of purified argon. After homogenization of the alloys at temperatures above the estimated liquidus temperatures, the samples were cooled, crushed, and ground to material that was 100 per cent below 100 mesh Tyler, and samples were taken for chemical analysis.

Differential Thermal Analyser

Constant rates of temperature programming were achieved by means of a Leeds and Northrup Series 60 current-adjusting control system. The temperature of the sample and the differential temperature were recorded continuously on a Leeds and Northrup Speedomax G two-pen recorder, the differential temperature signal being amplified. In addition, the sample temperature was recorded on a recording millivoltmeter in such a manner that, after a selected proportion of the output from the sample thermocouple has been suppressed, the cooling or heating curve could be monitored with a precision of 0,01 mV.

A vertical laboratory tube furnace wound with Pt-20 %Rh alloy was used. Provisions for atmosphere control was made by means of a gas-lock device. The argon gas, which was continuously passed through the system, was purified by spectrographic-grade argon passing over heated uranium turnings and through two microfilters.

The head assembly of the differential thermal analyser was modified so that one alumina crucible containing the alloy rested on a platinum dish attached to the sample thermocouple. The reference thermocouple was situated within the alumina head

in such a position that the temperature differential remained zero unless a reaction occurred in the sample. An earthed platinum sheath around the sample-holder block effectively screened out extraneous electromotive forces. Interference at the frequency of the mains supply was filtered out in the thermocouple circuit to the recorder.

Calibration of the Differential Thermal Analyser

Once the apparatus had been assembled and the correct geometry of the head assembly had been established so as to permit temperature programming while a zero temperature differential was maintained, the analyser was calibrated for several pure metals. The results indicated very good accuracy and precision, i.e., the accepted liquidus temperatures for gold, silver, copper, and nickel could be obtained with a precision of $\pm 5^\circ\text{C}$. Several test runs were then conducted so that the optimum rate of temperature programming for the ferrochromium-silicide alloys could then be established. A heating and cooling programme rate of 9°C per minute with a 5 g sample produced maximum sensitivity, but a considerable degree of supercooling occurred. The liqui-

us temperatures were therefore derived from the heating portions of the differential thermal analysis and from the amplified heating and cooling curves of the sample.

Classical Quench Method

When the liquidus temperature for each of the alloys had been derived from the thermal analysis, those temperatures were verified by the classical quench method. One-gram samples of the alloy were sealed into silica ampoules under low pressures of argon. These ampoules were suspended in a molybdenum-wound resistance furnace and, after being heated to 15°C above or below the liquidus temperature, as indicated from the thermal analysis, and held at the desired temperature, were quenched in a mixture of glycerine and water. The quenched specimens were mounted in epoxy resin and etched in a solution of 17 per cent nitric acid, 33 per cent hydrofluoric acid, and 50 per cent glycerol, and were examined under the microscope so that it could be established whether the microstructure contained a primary crystalline phase in a quenched matrix. In this manner it was possible for the liquidus temperatures to be determined to approximately 20°C .

TABLE I
The chemical compositions and liquidus temperatures of the ferrochromium-silicide alloys

Alloy number	Composition			Liquidus temperature °C
	Cr %	Fe %	Si %	
A ₁	40,4	10,1	50,5	1 422
A ₂	43,4	10,6	44,5	1 422
A ₃	46,5	12,1	40,5	1 423
B ₀	31,9	13,5	55,0	1 398
B ₁	34,2	15,6	49,5	1 394
B ₂	34,2	17,7	45,3	1 384
B ₃	41,2	18,5	39,8	1 410
B ₄	44,8	20,3	35,0	1 421
B ₅	49,2	21,6	29,8	1 497
C ₀	27,0	18,7	53,8	1 359
C ₁	29,8	20,7	48,9	1 367
C ₂	32,3	22,2	44,4	1 356
C ₃	35,2	24,2	40,0	1 400
C ₄	37,9	26,9	34,6	1 427
C ₅	40,9	28,4	30,0	1 447
C ₆	44,4	30,7	24,7	1 476
D ₀	22,5	22,8	54,0	1 323
D ₁	24,8	25,9	49,0	1 324
D ₂	27,5	27,8	44,3	1 317
D ₃	29,9	31,0	38,7	1 376
E ₁	19,9	30,3	49,3	1 295

Liquidus Temperatures

Table I incorporates the compositions of the alloys and the liquidus temperatures that were derived from the thermal analysis. In each instance, quenching from a temperature 15°C higher than the liquidus temperature evaluated from the thermal analysis, produced a microstructure indicative of a quenched liquid alloy, whereas quenching from a temperature 15°C lower produced a microstructure in which a crystalline primary phase could be identified.

The results are presented as liquidus curves on pseudo-binary sections at various ratios of chromium to iron in Fig. 1. The liquidus isotherms in the ternary system are shown in Fig. 2.

CONCLUSION

The liquidus temperatures of ferrochromium-silicide alloys generally are lowered with an increase in silicon content of 25 to 45 per cent. Higher silicon contents raise the liquidus temperatures slightly. As the ratio of chromium to iron in the alloys is increased, the liquidus temperatures are raised irrespective of the silicon content.

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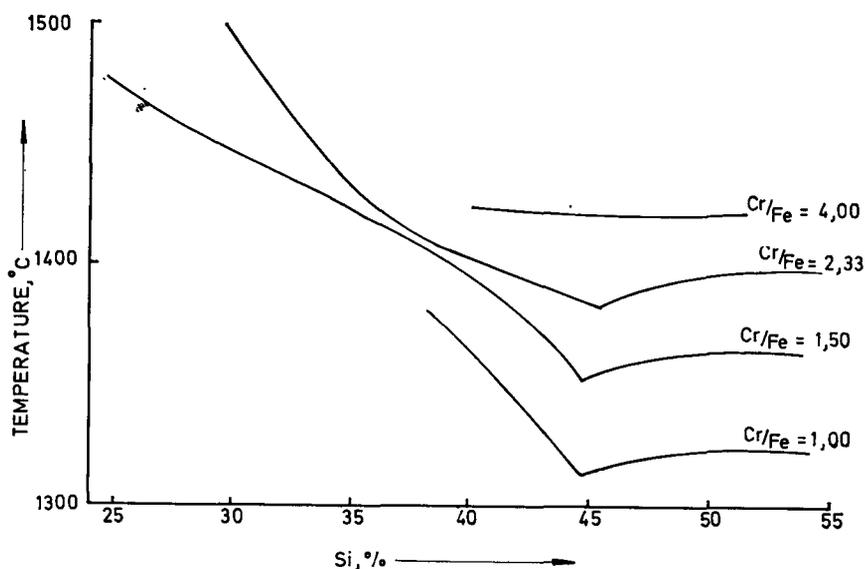


Fig. 1—Liquidus curves on pseudo-binary sections at selected ratios of chromium to iron

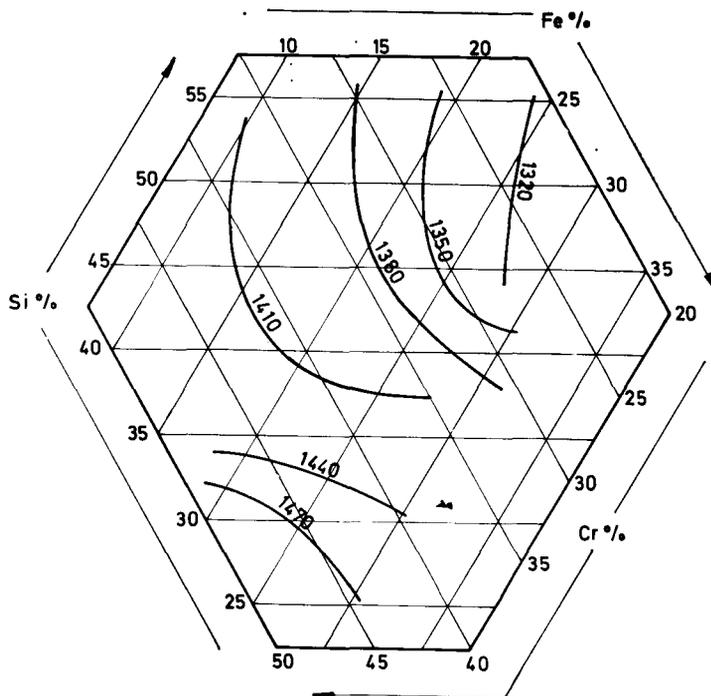


Fig. 2—Liquidus isotherms in the composition range representative of ferrochromium-silicide alloys