Phase Equilibria in the Cr–Fe–Si–C System in the Composition Range Representative of High-Carbon Ferrochromium Alloys Produced in South Africa

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Alloys in the composition range of Cr 50–65, Si 0–10, C 4–8%, balance Fe were subjected to differential thermal analysis, the classical quench method, microscopic examination, X-ray diffraction and electron-microprobe analysis. The liquidus temperatures and a considerable proportion of the phase constitutions have been determined for these alloys. The primary phase is $(Cr,Fe)_7C_3$ over the entire range of alloys investigated. Two pseudo-binary eutectics were identified; these eutectic reactions result in the formation of $(Cr,Fe)_7C_3$ and either α- or γ-iron–chromium solid solution, together with a eutectic reaction, which results in the formation of γ-iron–chromium solid solution and $(Cr,Fe)_{23}C_6$. There is a peritectic reaction between liquid alloy and $(Cr,Fe)_7C_3$ that yields $(Cr,Fe)_{23}C_6$, and a peritectoid reaction in which $(Cr,Fe)_7C_3$ and α-iron–chromium solid solution react to form $(Cr,Fe)_{23}C_6$. Those phases that contain silicon have been identified.

The production of high-carbon ferrochromium is accomplished by the smelting of chromite ore, together with reducing agent (coke, char, or coal), and fluxes (magnesite, dolomite, serpentine, and silica) in an electric smelting furnace. An important factor in the optimization of the smelting process is the relation between the liquidus temperature of the alloy and that of the slag. Once the burden components have reached the smelting zone, and have reacted and fused, the reaction products—alloy and slag—will drop away from the area of intense heat surrounding the electrode tips and settle to the furnace hearth. Consequently, if the alloy is to be superheated to the required degree, the slag must possess such a liquidus temperature and viscosity that it, together with the alloy, can only drain away from the arc zone when the alloy has attained the desired superheat required for subsequent tapping. Conversely, if the alloy is tapped at an excessively high temperature, the consumption of electric power and the rate of refractory wear increase. Hence, a knowledge of the liquidus temperatures of the high-carbon ferrochromium alloys is essential for both metallurgical and economic operation. The temperature interval between liquidus and solidus tempera-

tures is also important for the subsequent casting processes. Phase-constitution data are required if phase assemblages that are rich in chromium, carbon and silicon are to be defined. It is possible for the chromium content of ferrochromium to be increased by controlled cooling from the liquid state followed by a separation process to yield a low- and high-chromium fraction.[1] To understand the smelting reactions, and to determine the effect of the silicon content on the breaking strengths of the alloys, require a detailed knowledge of the phase constitution of the alloys.

The binary phase relations of the system Cr–Fe–Si–C have been reported by Hansen.[2] The ternary phase relations in the Fe–C–Si system have been investigated by Kriz and Poboril[3,4] and Honda and Murakami.[5] The ternary phase relations in the Fe–Cr–C system have been investigated by Austin,[6] Goerens and Stadeler,[7] Murakami,[8] Russel,[9] Westgren et al.,[10] and Griffing et al.[11] The ternary phase relations in the Fe–Cr–Si system have been investigated by Denecke,[12] Anderson and Jetté,[13,14] Sveshnikov and Alferova,[15] Elyutin et al.,[16] Kurnakov,[17,18] Dubrovskaya and Gel'd,[19] Petrushevskii,[20] and Gladyshevskii and Borusevich.[21] The quaternary phase relations have not been investigated apart from information derived from studies of the solubility of carbon in Cr–Fe–Si alloys by Lucas and Wentrup,[22] Jetté and Anderson,[23] Kurnkakov,[24,25] Caron,[26] Kadarmetov,[27] and Petrushevskii and Gel'd.[28]

Because of the relatively low ratio of chromium to iron in chromite ores in South Africa, the following range of alloy composition was selected as representative of high-carbon ferrochromium alloys produced from local ores: Cr 50–65, Si 0–10, C 4–8%, balance Fe.

Experimental

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

Sample Preparation

The compositions of the alloys were so selected that the quaternary system could be divided into five pseudo-ternary sections at carbon levels of 4, 5, 6, 7, and 8%. Alloys representative of three levels of silicon concentration, viz., 0, 5, and 10%, and four specified chromium-to-iron ratios were selected at each carbon level.

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 atmo-

sphere of purified argon. After the alloys had been homogenized by holding at temperatures above the estimated liquidus temperatures, the samples of alloy were cooled and then crushed and ground to material that was 100% 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, in which the differential temperature signal was amplified. In addition, the sample temperature was recorded on a recording millivolt-meter in such a manner that, after suppression of a selected proportion of the output of the sample thermocouple, the cooling or heating curve could be monitored with a precision of 0·01 mV.

Two furnaces were used for the differential thermal analysis. For temperatures below 1600°C a vertical laboratory tube furnace, wound with Pt–20%Rh alloy, was used, whereas for higher temperatures a molybdenum-wound furnace was constructed. Provision for atmosphere control was made by means of a gas-lock device. The argon gas, which was passed continuously through the system, was purified by the passing of spectrographic-grade argon over heated uranium metal turnings and through two microfilters.

The head assembly of the differential thermal analyser was modified so that one alumina crucible, which contained the alloy, rested on a platinum dish that was 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 spurious 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 was assembled and the correct geometry of the head assembly was established to permit temperature programming while a zero differential temperature was maintained, the analyser was calibrated with 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 ± 5 degC. Several test runs were then conducted so that the optimum rate of temperature programming for the high-carbon ferrochromium alloys could be established. A temperature programme rate of 9°C/min with a 5 g sample produced maximum sensitivity with relatively low thermal lag.

Liquidus temperatures of the alloys during the testing programme were found to be higher on heating than on cooling. Supercooling of the order of 15 to 20°C was obtained, and this was verified by quenching specimens of the alloy from above and below the liquidus temperatures as given by heating and cooling curves. Jackson[29] has shown that the freezing-point of $(Cr,Fe)_7C_3$ was depressed by 2·0°C per °C per minute during cooling, i.e., 18°C for cooling rate of 9°C/min, and this was confirmed in this investigation.

The Classical Quench Method

When the differential thermograms for heating and cooling had been obtained for each of the alloy samples, the reaction temperatures were verified by use of the classical quench method. One-gramme 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 heating to above or below a particular reaction temperature, followed by equilibration at the desired temperature (normally 15°C above or below the reaction temperature as indicated by the differential thermal analysis), were quenched into a mixture of glycerine and water.

The quenched specimens were mounted in epoxy resin and etched, in a 50% solution of boiling hydrochloric acid. Microscopic examination, X-ray diffraction, and electron-microprobe analysis were then conducted.

Electron-Microprobe Analysis

The individual phases were analysed by the electron-microprobe. The results are presented in Table I. Only the chrome, iron, and silicon contents were analysed, whereas the carbon was calculated by difference. The precision of the analytical data for the three elements is ±2 units on the quoted figures.

Table I   Results of the electron-microprobe analysis

Alloy composition			Primary carbide				Eutectic carbide				Peritectic carbide				Matrix phase			
Cr:Fe ratio	Si, %	C, %	Cr, %	Fe, %	Si, %	C, %	Cr, %	Fe, %	Si, %	C, %	Cr, %	Fe, %	Si, %	C, %	Cr, %	Fe, %	Si, %	C, %
1·22	0·11	6·00	73	18	—	9	72	19	—	9					24	78	—	—
2·17	0·03	8·02	67	23	—	9	62	29	—	9					19	83	—	—
1·49	9·66	4·05	81	12	—	7	44	31	21	4	60	27	10	4	19	69	13	—
											*60	27	9	4	17	71	13	—
											*57	29	10	4	18	70	13	—
1·57	9·28	6·00	71	20	—	8	44	35	18	3	54	33	11	2	17	70	16	—
			*71	20	—	8	43	36	17	4	54	33	11	2	17	71	15	—
1·33	4·70	7·03	70	21	—	8	39	48	8	5	43	44	8	5	12	78	12	—
															*11	77	12	—
1·18	4·75	3·98	80	12	—	8	79	12	—	9					35	58	7	—
1·85	4·15	5·00	81	11	—	8	54	34	6	6					51	39	8	2
							*49	37	7	7					*33	60	9	—
							*54	35	6	5								

* Duplicate analyses of a similar phase in the same alloy

1 *Liquidus isotherms in °C at selected carbon levels:* (a) 4%C; (b) 5%C; (c) 6%C; (d) 7%C; (e) 8%C.

Phase Constitution

The differential thermal analysis of all the alloy samples and the examination of some 250 quenched specimens permit the evaluation of the liquidus temperatures, and also of a considerable proportion of the phase constitution.

Liquidus Temperatures

From the results derived from the differential thermal analysis and the classical quench method experiments, the pseudo-ternary liquidus diagram can be plotted at various carbon levels. These are presented in Figs. 1(a)–(e). It is estimated that these liquidus temperatures are correct to ±15°C. This value was derived from a consideration of the accuracy and precision of the thermal analysis and of the classical quench method, and takes account of slight errors in the analysis of the alloys.

At all carbon levels, an increase in the chromium content (and therefore a decrease in the iron content) is associated with an increase in liquidus temperature, and this is more pronounced in those alloys with higher carbon contents. The general increase in liquidus temperature with an increase in carbon content is in agreement with the chromium–carbon and iron–carbon binary diagrams, both of which reflected a rapid increase in liquidus temperature with an increase in carbon content >4%. At the higher carbon contents, an increase in the silicon content decreases the liquidus temperature. However, at the lower carbon contents, the liquidus temperature decreases with additions of silicon only in excess of 5%, and additions from 0 to 5% increase the liquidus temperatures.

The Primary Crystallizing Phase

Over the entire range of alloy composition investigated, the primary phase crystallizing from the melt is the trigonal carbide $(Cr,Fe)_7C_3$. Electron-microprobe analysis of this carbide indicates that this phase does not contain silicon. This carbide is essentially a chromium carbide in which up to 55% of the chromium atoms can be replaced by iron atoms.[10] Pseudo-binary sections, presented as temperature against the ratio of chromium to iron for selected constant silicon and carbon levels, are shown in Fig. 2. The accuracy of these results is estimated to be ±20 degC, since reaction temperatures, as indicated by differential thermal analysis, were confirmed by quenching experiments at 15 degC above and below these temperatures. The errors attributable to the thermocouple and temperature gradients of the quenching furnace were estimated at ±5 degC.

### The Second Phase to Appear from the Liquid Melt on Cooling

The $(Cr,Fe)_7C_3$–Chromium Solid Solution Eutectic

In those alloys that do not contain silicon, the second reaction results in the formation of a pseudo-binary eutectic involving either α (bcc) or γ (fcc) chromium solid solution together with $(Cr,Fe)_7C_3$. Both the carbon content and ratio of chromium to iron determine whether the solid solution is α or γ. Hence, at the 4 and 5% carbon levels the solid solution phase in the eutectic is α, whereas in the 7 and 8% carbon levels γ solid solution replaces the α. However, at the 6% carbon level, those alloys with higher ratios of chromium to iron contain α and those alloys with lower ratios of chromium to iron contain γ solid solution in the eutectic. The analysis of the carbide in this eutectic has been shown to be similar to the primary carbide. This change from α to γ solid solution in the eutectic with $(Cr,Fe)_7C_3$ as a function of carbon content and the ratio of chromium to iron in alloys with no silicon is in
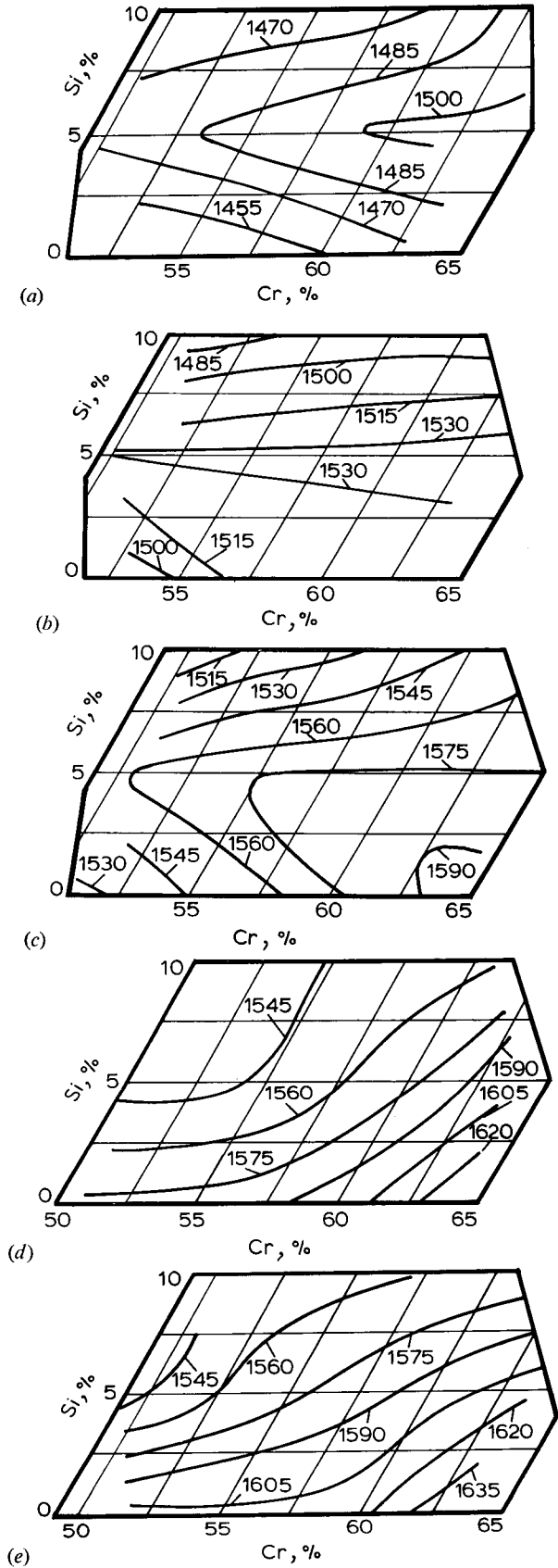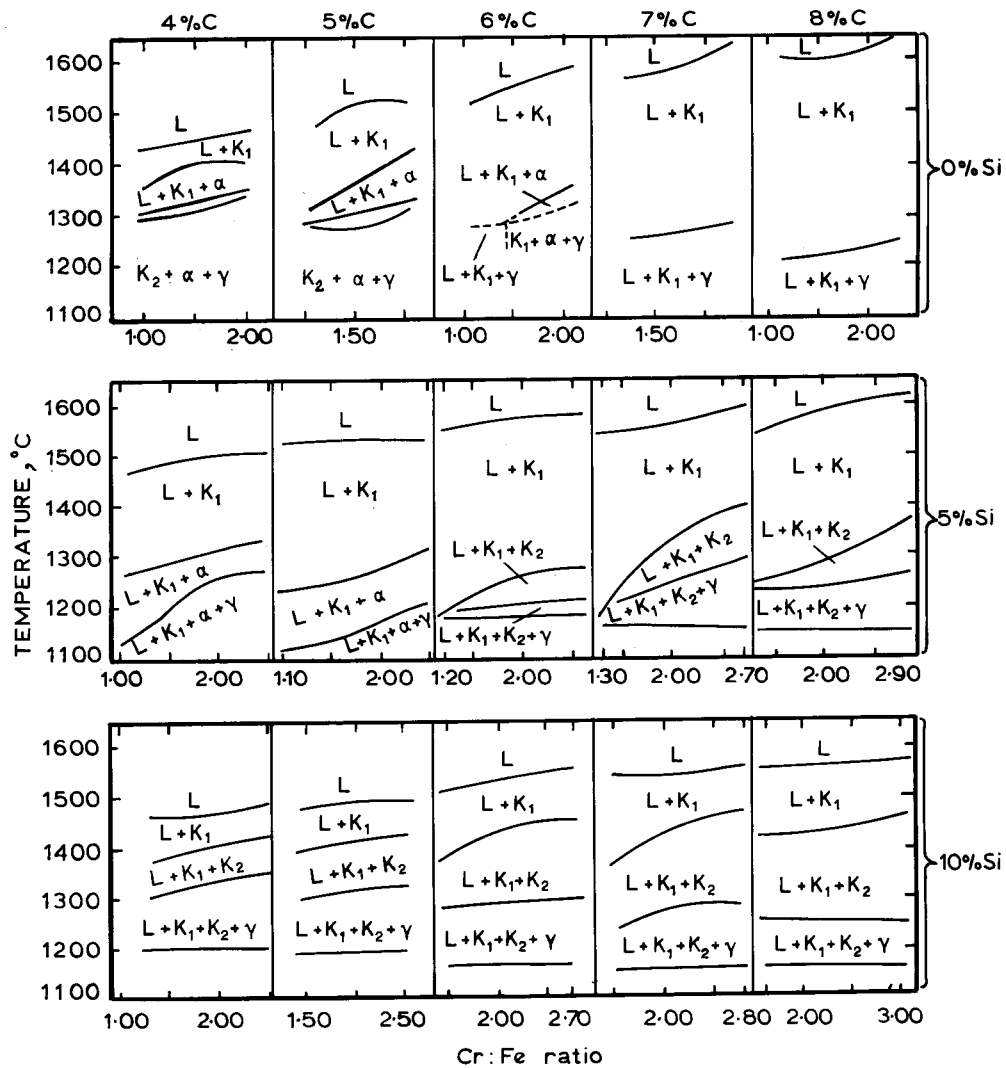
2 *Pseudo-binary sections at selected constant silicon and carbon contents. KEY: L = liquid $K_1 = (Cr,Fe)_7C_3$*
$K_2 = (Cr,Fe)_{23}C_6$ $\alpha = \alpha$-iron–chromium solid solution $\gamma = \gamma$-iron–chromium solid solution.

accordance with the Fe–Cr–C ternary phase diagram of Griffing et al.[11] This eutectic has a needle-like morphology.

Alloys at the 4 and 5% carbon levels, and containing 5% silicon, exhibit a similar secondary reaction, resulting in the crystallization of $(Cr,Fe)_7C_3$ and α solid solution, but electron-microprobe analysis showed that the α solid solution contained silicon.

The Peritectic Formation of $(Cr,Fe)_{23}C_6$

All alloys with 10% silicon, and those alloys at the 6, 7, and 8% carbon levels that contain 5% silicon, exhibit a peritectic reaction between liquid alloy and $(Cr,Fe)_7C_3$, i.e., liquid + $(Cr,Fe)_7C_3 \rightarrow (Cr,Fe)_{23}C_6$. This $M_{23}C_6$ type carbide is essentially a cubic chromium carbide in which up to 25% of the chromium atoms can be replaced by iron atoms.[10] This phase contains silicon, the amount depending on the amount of silicon present in the alloy. It appears feasible that the silicon exists in the carbide as a silicide.

**The Third Phases to Crystallize from the Melt**

Gamma Solid Solution

In the alloys that have a secondary reaction which results in the formation of $(Cr,Fe)_7C_3$ and α solid solution as a pseudo-

binary eutectic, γ solid solution crystallizes in a subsequent ternary reaction. The proportion of this phase is so small that positive identification by X-ray diffraction was not feasible. According to Griffing et al.[11] and Jackson,[29] this γ solid solution is the product of a peritectic reaction. This phase, like the α crystallizing before it, contains silicon if silicon is present in the alloy.

The $(Cr,Fe)_{23}C_6–\gamma$ Solid Solution Eutectic

The alloys that have a secondary reaction in which $(Cr,Fe)_{23}C_6$ is formed as a result of a peritectic reaction undergo a third reaction in which γ solid solution and $(Cr,Fe)_{23}C_6$ crystallize as the result of a eutectic reaction. Both these phases were shown to contain silicon, the proportion of silicon being dependent on the silicon content of the alloy. The microstructure of this eutectic exhibits a typical 'Chinese script' appearance.

In those alloys where $(Cr,Fe)_7C_3$ and γ solid solution are the products of a secondary eutectic reaction there is no further evidence of reaction nor could the presence of a tertiary phase be established by microscopic examination. Theoretically a third reaction should occur.
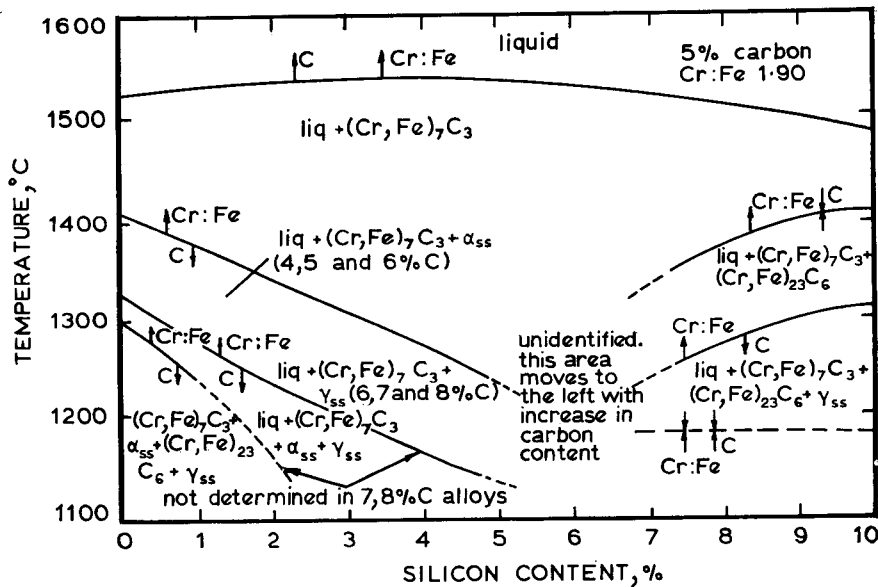
3 *Pseudo-binary section showing the trends in phase constitution with changes in the Cr : Fe ratio and carbon content. KEY: ↑C = increase in reaction temperature/increase in carbon content ↓C = decrease in reaction temperature/increase in carbon content ↑Cr:Fe = increase in reaction temperature/increase in Cr:Fe ratio ↓Cr:Fe = decrease in reaction temperature/ increase in Cr:Fe ratio ↯C or ↯Cr:Fe = no significant change in reaction temperature/ increase or decrease in carbon content or Cr:Fe ratio.*

The Peritectic Formation of (Cr,Fe)₂₃C₆

Alloys having a carbon content of 4 and 5% and no silicon exhibit a fourth reaction that is a peritectoid reaction in which (Cr,Fe)₇C₃ and α solid solution react to form (Cr,Fe)₂₃C₆. This reaction not only involves the primary carbide (Cr,Fe)₇C₃ but also the carbide in the eutectic.

Although most alloys that contain silicon exhibited a fourth reaction temperature on the differential thermal analyser, the reaction could not be identified because insufficient reaction phase was produced. Some of the alloys in which the silicon content was 5% exhibited no fourth reaction temperature on the thermal analyser, although from phase-rule considerations a fourth reaction should take place. Microscopic examination also failed to reveal a fourth reaction.

Conclusions

The phase relations, as far as they have been established, can be generally described with reference to the individual diagrams in Fig. 2. For ease of reference Fig. 3, which is based on the assumption of a pseudo-binary system comprising silicon content against temperature, has been prepared. The liquidus temperatures of the alloys are increased by increase both in carbon content and ratios of chromium to iron. The primary phase is (Cr,Fe)₇C₃ over the entire range of alloys investigated. The temperature interval over which this primary phase crystallizes increases with an increase in carbon content and the ratio of chromium to iron.

The alloys that have a 4 to 5% carbon content and at most only a trace of silicon follow similar crystallization patterns. The secondary reaction results in the formation of a eutectic containing (Cr,Fe)₇C₃ and α solid solution. The third reaction crystallizes γ solid solution, followed by a peritectoid reaction in which (Cr,Fe)₇C₃ and α solid solution react to form (Cr,Fe)₂₃C₆. The temperatures of the above three reactions are increased with an increase in the ratio of chromium to iron and are decreased with an increase in the carbon content.

The alloys that have a 7 or 8% carbon content and at most only traces of silicon exhibit a secondary reaction during which more (Cr,Fe)₇C₃ and γ solid solution are crystallized from the melt as a eutectic. The temperature of this reaction is raised by an increase in the ratio of chromium to iron and is lowered by an increase in the carbon content. No further reactions could be identified for these alloys. At all carbon levels the solid solution contains silicon if the alloy contains silicon.

The alloys that have a 6% carbon content, with no silicon or only small amounts of it, follow the same crystallization pattern as the alloys at the 7 and 8% carbon level if the ratio of chromium to iron is low.

At all carbon levels, alloys with the higher silicon contents exhibit similar subliquidus reactions. In the secondary reaction (Cr,Fe)₂₃C₆ is formed by a peritectic reaction between liquid alloy and (Cr,Fe)₇C₃. The reaction temperature increases with an increase in the ratio of chromium to iron but undergoes little change with a change in the carbon content. In the ternary reaction, which is of a eutectic type, γ solid solution and (Cr,Fe)₂₃C₆ are formed; both phases contain silicon. The reaction temperature is increased by an increase in the ratio of chromium to iron and is decreased by an increase in the carbon content. A quaternary reaction has been identified in some of the alloys by differential thermal analysis. The temperature of the reaction is not significantly affected by changes in the carbon content or the ratio of chromium to iron.

The unidentified subliquidus region in the centre of the diagram is shifted to the low silicon end with an increase in the carbon content.

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ROSENHAIN CENTENARY CONFERENCE

A MEETING TO CONSIDER

THE CONTRIBUTION OF PHYSICAL METALLURGY TO ENGINEERING PRACTICE

at The National Physical Laboratory, Teddington, and The Royal Society, London

22–24 September 1975

The centenary of the birth of Walter Rosenhain (1875–1934) will be celebrated by an international conference to consider how physical metallurgy has contributed to engineering practice. The value of an applied discipline such as metallurgy can be measured by its effect on practice. Few contributed more than Rosenhain to the development of the modern physical metallurgical approach; few applied it more effectively.

The aspects of engineering which will be considered at the conference will include bridges, linepipe, offshore structures, airframe structures, and gas turbines. Definition of engineering needs and how these relate to material characteristics will be followed by discussion on the success of metallurgical development in satisfying the demands made on suppliers of materials. Finally, there will be a summary of the implications for physical metallurgy and for the education and training of metallurgists, which arise from discussions at the conference.

Rosenhain was a Fellow of the Royal Society and an active member of both The Iron and Steel Institute and The Institute of Metals which are now combined in The Metals Society. He was also Superintendent of the Department of Metallurgy and Metallurgical Chemistry at the National Physical Laboratory, a post he held for 25 years.

The technical discussions will be held at the Royal Society but will be preceded by an exhibition at the National Physical Laboratory which will include current work as well as exhibits specifically relating to Rosenhain and his work. A special feature will be a lecture recalling Rosenhain's specific contributions to science and technology.

Social events will include a Conference Reception at the National Physical Laboratory, a Conference Dinner in London, and a full Ladies' Programme. Further details and registration forms can be obtained from the Conference Secretary (Rosenhain Centenary Conference), The Metals Society, 1 Carlton House Terrace, London SW1Y 5DB. The number of places is limited to 300, so early application is advised.