

Crystallization Processes in a High-carbon Ferrochromium Slag

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SYNOPSIS

The crystallization processes that take place during the cooling of a slag in the system $MA-M_2S-CAS_2-M_2A_2S_5$ (spinel—forsterite—anorthite—cordierite) have been examined and compared with the relevant phase equilibrium data. Spinel is shown to be the stable high-temperature phase up to about 1800°C. During cooling, spinel and forsterite crystallize from solution in the liquid phase. Small amounts of enstatite are also formed, and its presence is explained by arrested peritectic reactions. Heat treatment of the slags in the laboratory has been shown to take the peritectic reaction more nearly to completion. The practical importance of the presence of spinel at high temperature is discussed.

INTRODUCTION

Some years ago the writer¹ was able to show that the melting relationships proposed by Solacolu² for the system $MgO-MgO.Al_2O_3-2MgO.SiO_2-2CaO.SiO_2$ ($M-MA-M_2S-C_2S$, magnesia—spinel—forsterite—dicalcium silicate) could be used to describe the melting and crystallization processes that took place during the firing of refractory brick based on mixtures of magnesite (MgO) and chromium ore. Even though chromium oxides and iron oxides are present in the chrome spinel, the sequence of crystallization steps was very similar to that shown by the phase diagram of the pure-oxide system.

The diagram proposed by Solacolu is reproduced in Figure 1, in which the melting path of a composition approximating to that of a magnesite—chrome refractory is shown as the hatched line $DCBA$. During heating, the lime-rich quaternary peritectic of composition D melts at 1380°C, and with further heating the composition of the liquid moves along the hatched line DC as magnesia, forsterite, and some spinel are taken into solution. At C , in this instance 1525°C, the composition path of the liquid changes direction along CB , and spinel and magnesia are taken into solution simultaneously until at B (1600°C) all the spinel is in solution. With further rise of temperature above 1600°C, MgO only is taken into solution, until complete melting occurs well above 2000°C.

During cooling, the processes are reversed, and MgO , MgO plus spinel, and MgO plus spinel and forsterite, crystallize from solution along AB , BC , and CD , respectively. In a chrome—magnesite refractory, the spinel phase was shown to crystallize as angular particles, and the magnesia as separate spheroidal particles or onto existing magnesia grains. The mutual interference between the crystallizing phases gave rise to an interlocking structure of solid grains in contact, which was responsible for improved high-temperature mechanical strength and subsequent improved service performance. Increasing the firing temperature increased the total amount of spinel and magnesia taken into solution, and, on cooling, the total amount of bonding between phases in the fired brick was increased.

Even though liquid is present at a temperature as low as 1380°C, the system exhibits high refractoriness because of the continued presence, at high temperature, of primary MgO and undissolved spinel particles. The system is

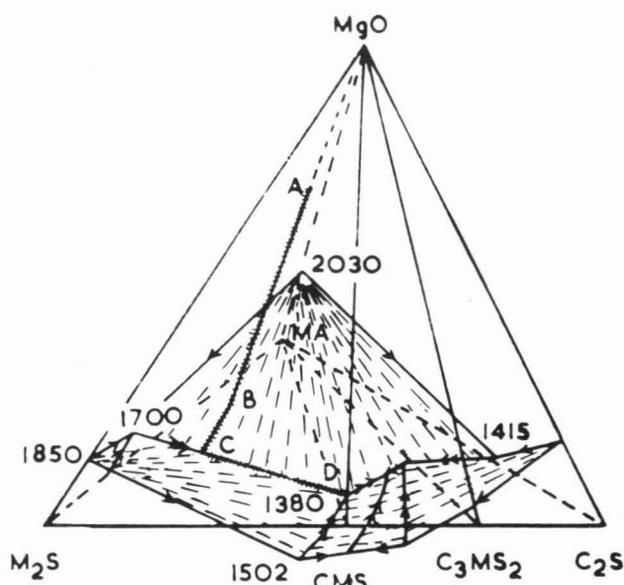


Figure 1

System $MgO-MgO.Al_2O_3-2MgO.SiO_2-2CaO.SiO_2$ after Solacolu²

characterized by fairly high temperatures of initial melt formation, long melting paths, and high final melt temperatures. Much further work has since been carried out on the solubility, in silicate melts, of spinels that contain both chromium and iron oxide. El Shahat and White³ showed that, in the $C_2S-(MA.MK.MF)$ and $CMS-(MA.MK.MF)$ systems, the presence of Cr_2O_3 in the spinel increased the temperature of initial liquid formation and also decreased the solubility of the spinel in the silicate liquid. When monticellite (CMS) was present, however, the effect was relatively small, the temperature of initial liquid formation being increased to only 1490°C compared with 1700°C when dicalcium silicate (C_2S) was present.

COMPOSITION OF HIGH-CARBON FERROCHROMIUM SLAGS

The phase assemblage described by Solacolu belongs to the larger $CaO-Al_2O_3-MgO-SiO_2$ system, which also describes the crystallization behaviour of ferrochromium slags. In this work, three somewhat experimental slags were chosen for examination. The contents of chromic oxide and alumina were high in all three slags, and the Cr_2O_3 was assumed to be present mainly as rela-

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tively unaltered chrome spinel or as ferrochromium metal. Chemical analysis of the slags was as follows:

	Cr ₂ O ₃	SiO ₂	CaO	MgO	Al ₂ O ₃
Slag 1	18,7	18,4	2,3	23,8	24,9
Slag 2	18,7	26,8	2,2	25,3	25,2
Slag 3	10,7	25,3	1,8	32,3	24,6

Recalculating the chemical analysis of the slags to zero Cr₂O₃ gave the following results:

	SiO ₂	CaO	MgO	Al ₂ O ₃
Slag 1	26,5	3,3	34,3	35,9
Slag 2	33,7	2,8	31,8	31,7
Slag 3	30,0	2,1	38,4	29,2

The calculated phase composition below shows that the slags fall within the quaternary tetrahedron MA—M₂S—CAS₂—M₂A₂S₅ (spinel—ferrosterite—anothite—cordierite).

	MgO·Al ₂ O ₃ (Spinel)	2MgO·SiO ₂ (Forsterite)	CaO·Al ₂ O ₃ ·2SiO ₂ (Anothite)	2MgO·2Al ₂ O ₃ ·5SiO ₂ (Cordierite)
Slag 1	39	40	16	5
Slag 2	26	37	14	23
Slag 3	31	50	11	8

Spinel and forsterite, which are both materials with high melting-points, are major phases in all three slags, and, because of this, the slags can be assumed to be fairly refractory. Cordierite is present in slags 1 and 3 in minor amounts only, but quite a small change in composition has given rise to a considerable amount in slag 2.

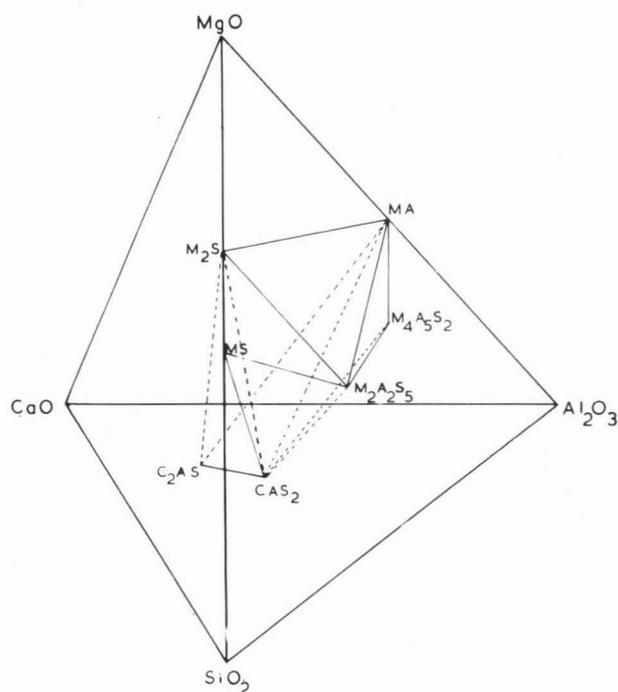


Figure 2

Phase assemblages within the system MgO—Al₂O₃—CaO—SiO₂

The position of the above tetrahedron in the Al₂O₃—CaO—MgO—SiO₂ system is shown in Figure 2. Figure 3 shows in an exploded form the positions of the adjacent compatibility tetrahedra, i.e.,

- M₂S—MA—CAS₂—C₂AS (gehlinite)
- M₂S—MS (enstatite—CAS₂—M₂A₂S₅)
- MA—CAS₂—M₂A₂S₅—M₄A₅S₂ (saphirine).

Within this area of the diagram, the field of primary spinel + liquid shows extensive stability, and an attempt has been made in Figure 3 to show the volumes within the four tetrahedra where spinel is stable at high temperature. It will be noted that spinel is the high-temperature phase over a wide range of compositions. The extent of the spinel phase field is also shown by the diagrams of Osborn, de Vries, Gee, and Kramer⁴, and, in Figure 4, the compositions of slags 2 and 3 are plotted on the 30 per cent Al₂O₃ diagram by the above authors. Similarly, the composition of slag 1 can be plotted on the diagram at 35 per cent Al₂O₃. All three compositions are clearly within the primary stability field of spinel plus liquid and, because of the low CaO content, fall close to the MgO—SiO₂—Al₂O₃ side of the tetrahedron.

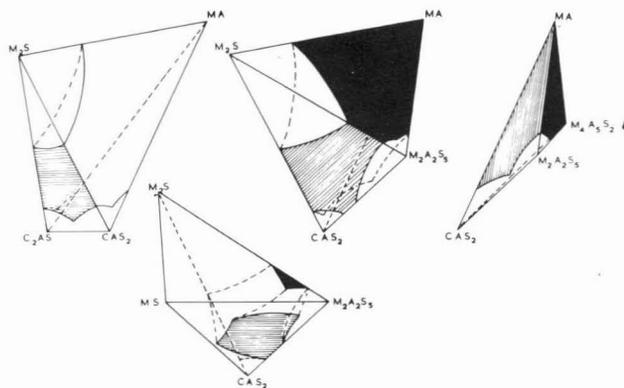


Figure 3

The phase assemblages shown in Figure 2 exploded and showing extent of spinel + liquid stability field at high temperature

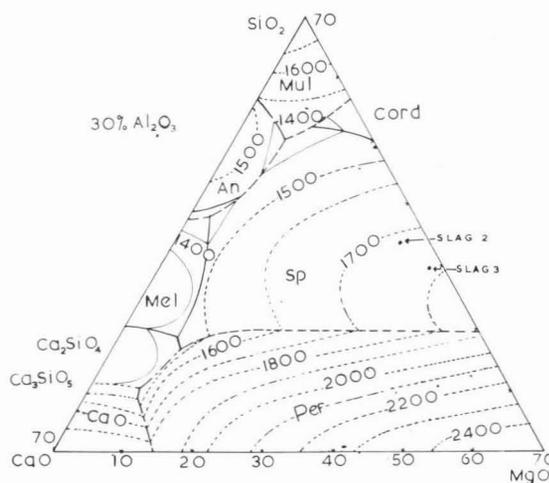


Figure 4

System MgO—Al₂O₃—CaO—SiO₂ at the 30 per cent and 35 per cent Al₂O₃ level, after Osborn, de Vries, Gee, and Kramer⁴, showing composition of slags from ferrochromium process

It is interesting to note at this stage that, in the $\text{Al}_2\text{O}_3\text{—CaO—MgO—SiO}_2$ system, enstatite (MS) is not a compatible phase with spinel. When Al_2O_3 is replaced by Cr_2O_3 , there is no chromium analogue of cordierite, so that the spinel phase ($\text{MgO} \cdot \text{Cr}_2\text{O}_3$) becomes compatible with enstatite (MS) as is shown in Figure 5.

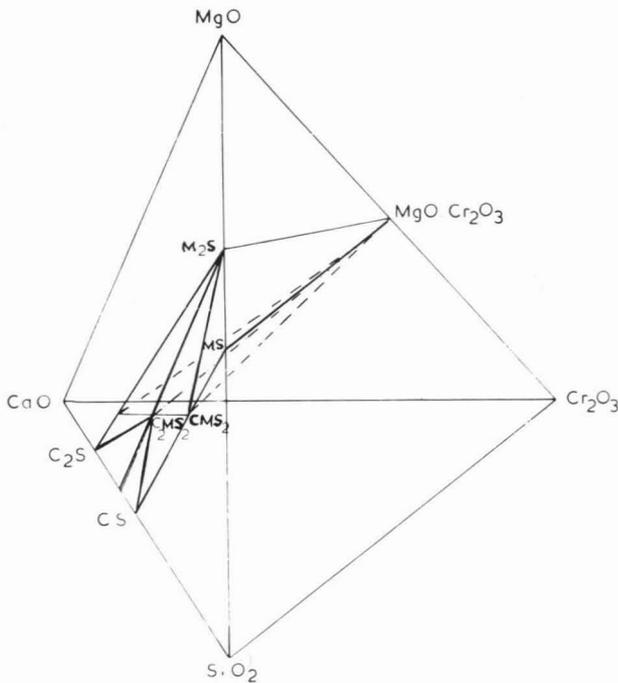


Figure 5

Phase assemblages in the system
 $\text{MgO—Cr}_2\text{O}_3\text{—CaO—SiO}_2$

X-RAY-DIFFRACTION EXAMINATION AND MICROSTRUCTURE

X-ray-diffraction examination of the three slag samples showed the presence of the following phases in each:

Major Phase: Spinel (lattice parameter 8,11 Å)
Forsterite (M_2S)

Secondary Phase: Spinel (lattice parameter 8,29 Å)
Chromium carbide (Cr_7C_3)
Enstatite ($\text{MgO} \cdot \text{SiO}_2$).

The major spinel present has a lattice parameter (8,11 Å) very close to that of pure $\text{MgO} \cdot \text{Al}_2\text{O}_3$ (lattice parameter 8,084 Å). The minor spinel phase (lattice parameter 8,29 Å) can be assumed to be unaltered chromium ore (lattice parameter 8,29 Å) because of the close agreement between lattice parameters. Peak heights on the X-ray-diffraction charts showed that the amount of unaltered chrome varies from fairly large amounts in slag 1 to only small amounts in slag 3, but no attempt was made in this work to carry out quantitative determinations. The presence of forsterite is as predicted; but enstatite is somewhat unexpected, and chromium carbide is presumably present as entrained ferrochromium.

Photomicrographs, of polished sections of the slags, that confirm the X-ray-diffraction findings are shown in Figures 6, 7, and 8. Unreduced chromium ore can be seen in all sections as rounded particles of relatively high reflectivity, the amount varying from large quantities in slag 1 to only occasional particles in slag 3. All the unreduced chromium-ore particles are surrounded by rims of angular spinel, which are of lower reflectivity, and angular spinel particles can also be seen throughout the matrix. Light-grey elongated crystals of forsterite can be

clearly seen between the spinel particles. At higher magnification (Figure 9), the rims of low-reflectivity angular spinel can be seen to be continuous with the unreduced chromium ore. The latter appears to be porous, and it is interesting to note the concentration of small metallic globules of ferrochromium at the junction of the two spinels and within the angular spinel rim. The glassy matrix between the spinel and forsterite particles contains small, light-grey, lath-shaped crystals thought to be the enstatite detected by X-ray diffraction.



Figure 6

Microstructure of slag 1 at low magnification. Particles of unreduced chromium ore (C) are surrounded by spinel (Sp) of lower reflectivity. Angular crystals of forsterite are present in the matrix.

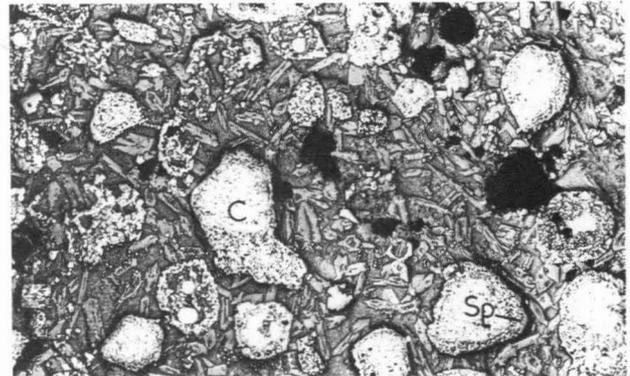


Figure 7

Microstructure of slag 2 at low magnification. Fewer unreduced chromium-ore particles are present.

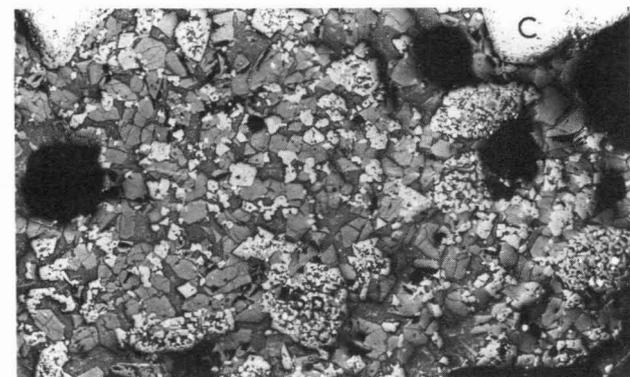


Figure 8

Microstructure of slag 3 at low magnification. Few particles of unreduced chromium ore are present, but the matrix contains large amounts of small angular spinel crystals (Sp).

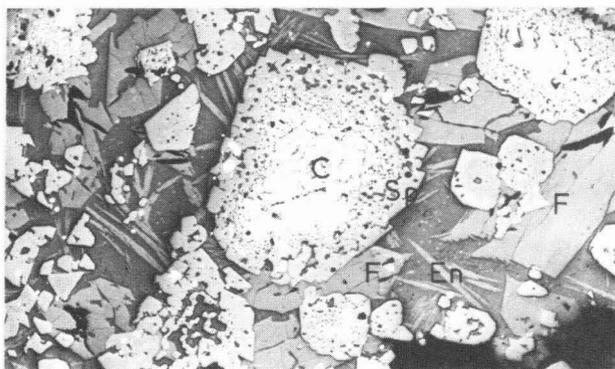


Figure 9

Microstructure of slag 1 at higher magnification. Particles of unreduced chromium (C) surrounded by angular spinel (Sp) of low reflectivity containing globules of metallic ferrochromium. Lath-shaped crystals of enstatite (En) can be seen in the glassy matrix between the angular forsterite crystals (F).

HEAT TREATMENT OF SLAG SAMPLES

The presence of glass in the slag samples shows that crystallization has been incomplete, and so, to complete the crystallization process, one-inch lumps of slag were heated to 1250°C in the laboratory for 24 hours and then slowly cooled to 1000°C over a period of about 5 days. Above 1250°C, only a thin layer on the surface of the sample was obviously oxidized and the interior of the sample appeared to be unaffected. X-ray diffraction was again carried out on samples from the interior of the slowly cooled samples and polished sections prepared, giving the following results:

- Major Phases: Spinel (lattice parameter 8,11 Å)
 Forsterite (M₂S)
 Enstatite (MS)
 Anorthite (CAS₂)
- Minor Phases: Spinel (lattice parameter 8,29 Å)
 Chromium carbide (Cr₇C₃).

Both anorthite and more enstatite had formed in relatively large amounts during the heat treatment and slow cooling.

Polished sections (Figure 10) show the elongated forsterite crystals covered with rims of smaller enstatite crystals that had formed during the heat-treatment process.

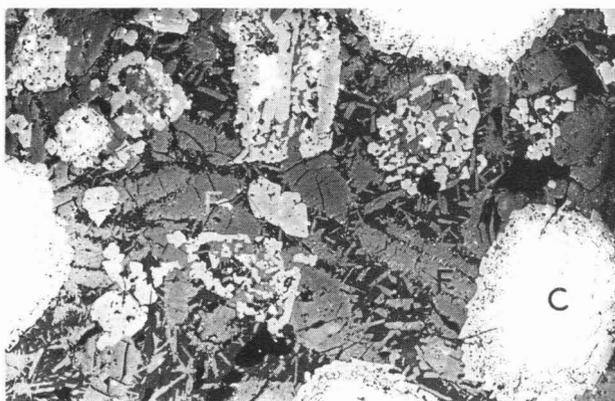


Figure 10

Microstructure of slag 1 heated to 1250°C and slowly cooled. Peritectic rims of enstatite have formed on the forsterite crystals (F), and some of the angularity of the angular spinel has been lost.

These can be seen more clearly at higher magnification (Figure 11), and the previously glassy matrix now contains angular crystals of anorthite. Closer examination of Figure 10 indicates that many of the smaller angular spinel crystals have disappeared during heat treatment, and rims of spinel round the chromium-ore particles have become more irregular (compare with Figure 9).

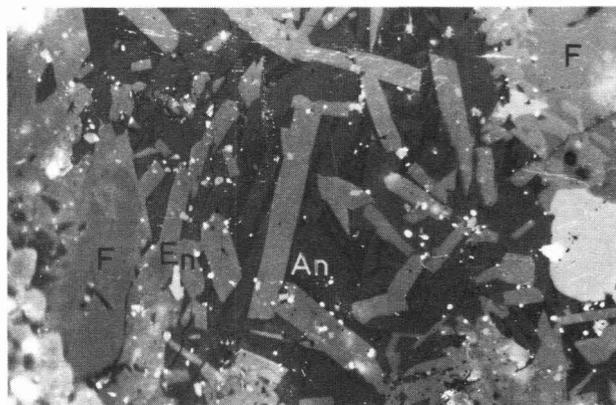


Figure 11

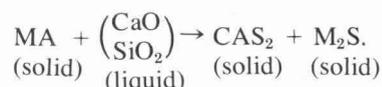
Microstructure of heat-treated slag at higher magnification. Crystals of forsterite (F) with peritectic rims of enstatite (En) and matrix now crystallized as anorthite (An).

CRYSTALLIZATION PROCESSES

The melting and crystallization behaviour of the slag can be explained by examination of the melting relationships in the quaternary system Al₂O₃—CaO—MgO—SiO₂. Details of this system are given by Chinner and Schairer⁵, but, since only a small amount of cordierite is present, it is possible to show the melting and crystallization paths in the simpler subsystems MA—M₂S—CAS₂, M₂S—CAS₂—MS, and MS—CAS₂—SiO₂. Melting relationships in the above systems are shown in Figure 12, for which all the information was obtained from existing data⁶.

As in the quaternary system (Figure 3), the range of composition over which spinel is stable at high temperature is large, and in Figure 12 the spinel and liquid field spreads from the MA—M₂S side of the diagram across the MA—M₂S—CAS₂ triangle in such a way that the peritectic point *d* lies well within the adjacent triangle M₂S—CAS₂—MS.

The compositions of the three slags are plotted in Figure 12 as points 1, 2, and 3, respectively. Above about 1800°C, all three slags are completely liquid, but, during cooling, precipitation of spinel commences from slag 1 at about 1850°C. With further cooling, the composition of the liquid phase moves along the hatched lines until the valley line is met at *bd*, i.e., approximately 1675°C for slag 1. Increasing amounts of spinel crystallize during cooling. At 1675°C (slag 1), the crystallization path changes direction along the valley line towards *d*, precipitating spinel and forsterite simultaneously until the liquid composition reaches *d* at 1340°C. At *d*, freezing would normally be completed by the peritectic reaction between the lime-rich liquid and the solid spinel to give anorthite and more forsterite:



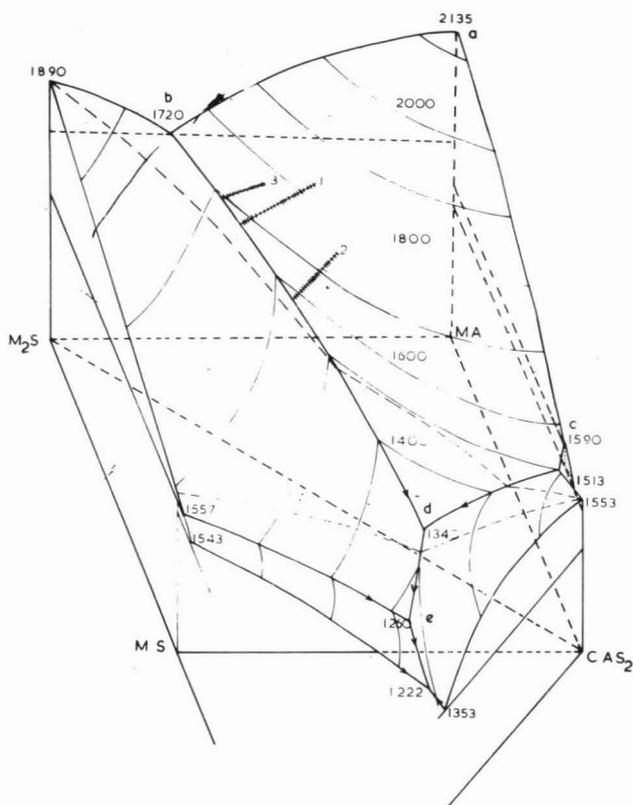
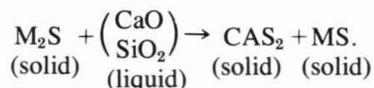


Figure 12

Melting relationships in the system $MA-M_2S-CAS_2$, M_2S-CAS_2-MS , and $MS-CAS_2-SiO_2$.

Peritectic reactions in oxide systems are, however, slow, and during rapid cooling the peritectic reaction may be arrested and the lime-rich liquid will continue freezing along *de*, with anorthite and forsterite being precipitated direct from the liquid. At *e* (1260°C), a second peritectic reaction would normally take place, this time between the lime-rich liquid and forsterite to give enstatite and anorthite:



It can be seen that point *e* lies within a third triangle $MS-CAS_2-SiO_2$, and the peritectic reaction above may again be arrested by rapid cooling, freezing not being completed until the ternary eutectic point at 1222°C is reached. In practice, the final liquid will probably solidify as a glassy material since much of the direct precipitation from the liquid phase will be suppressed.

Slag 2 shows complete melting at about 100°C lower than slag 1 (i.e., 1750°C), and forsterite is not precipitated until about 1575°C; but otherwise a similar crystallization path is followed. The rather lower temperatures of complete melting would indicate a more workable slag, and this was actually found in practice.

Figure 13 is included to show diagrammatically the horizontal peritectic reaction planes connected to *d* and *e* and also the eutectic plane at 1222°C. These planes are again reproduced in Figures 14 and 15 and can be used for determining the reaction sequence that will take place as the temperature passes through 1340°C and 1260°C respectively. For instance, above 1340°C (Figure 14) the composition of the slags falls in the triangle marked

$M_2S+MA+L$. Below 1340°C the compositions fall within the triangle $M_2S+MA+CAS_2$. The proportions of the different phases can be computed⁷, but, in practice, at 1340°C the amount of spinel will decrease by reaction with the lime-rich liquid to give anorthite and more forsterite. This reaction has, in fact, taken place during the heat-treatment experiment, i.e., the smaller angular spinel crystals have dissolved and anorthite has been formed. The larger angular spinel crystals have also been involved in the reaction and have lost their previous angularity.

At 1260°C, Figure 15 shows, M_2S+CAS_2 +liquid reacts to give M_2S+CAS_2+MS , i.e. the liquid phase reacts with the forsterite, removing some of it from the system and giving enstatite and more CAS_2 . This reaction is also seen in the heat-treated samples, i.e., Figure 10 shows the forsterite crystals to be surrounded by reaction

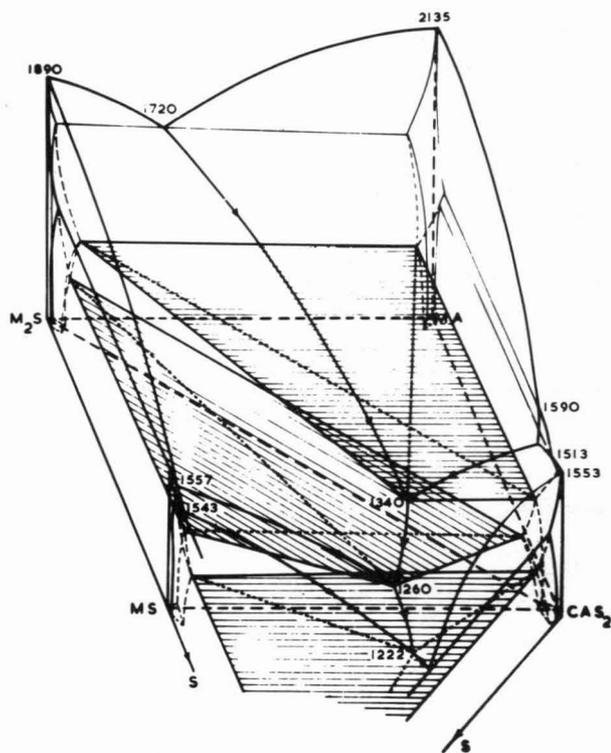


Figure 13

Diagrammatic representation of peritectic and eutectic planes in the systems $MA-M_2S-CAS_2$, M_2S-CAS_2-MS , and $MS-CAS_2-SiO_2$

rims of enstatite. Thus, although enstatite would not have been predicted from the slag analysis, its presence within the slag can be explained by the effect of arrested peritectic reactions.

DISCUSSION

The phase diagrams of the $MA-M_2S-CAS_2$ and $M_2S-MS-CAS_2$ systems show that, when a fully crystallized slag is heated, the spinel components will be taken into solution by the silicate liquid formed at the peritectic temperature 1340°C, although in practice some liquid

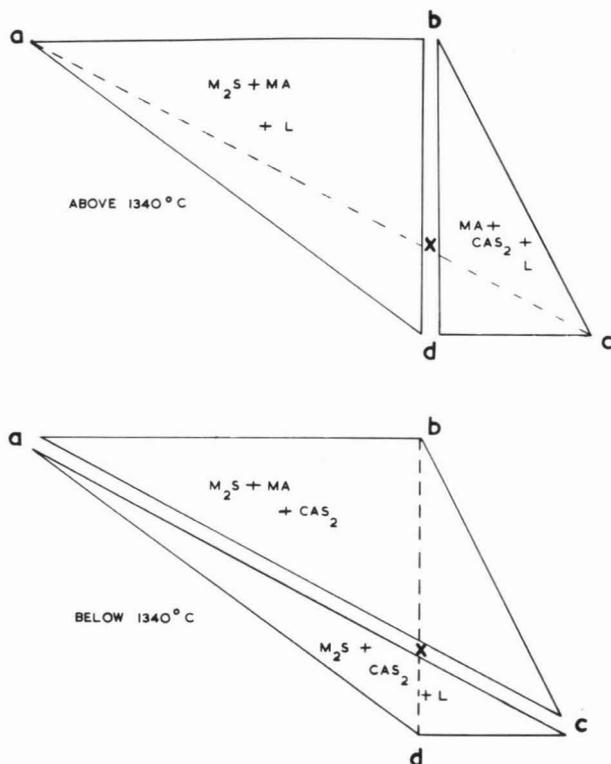


Figure 14

Peritectic plane at 1340°C showing reaction sequence

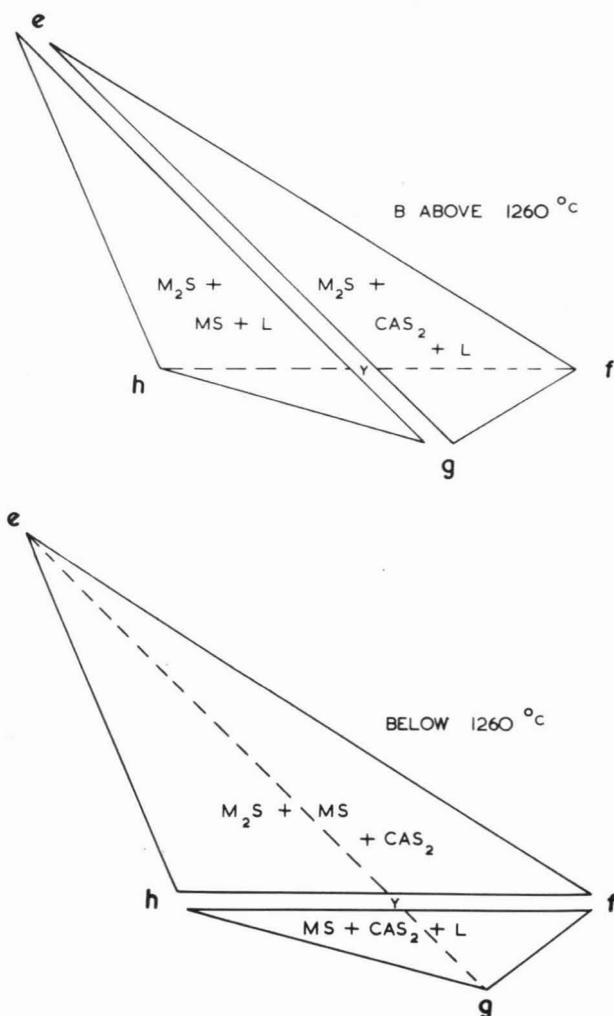


Figure 15

Peritectic plane at 1260°C showing reaction sequence

may be formed as low as the eutectic temperature of 1222°C. When cordierite is present, the peritectic temperature is lowered⁵ to 1280°C, but, when only small amounts of CaO are present, only small amounts of liquid form at this temperature. With increase of temperature above 1340°C, spinel continues to be dissolved until dissolution is complete at temperatures of the order of 1750 to 1850°C. As in the refractory systems examined by White, when Cr₂O₃ is present in the spinel phase it can be assumed that the temperature of initial melt formation will be increased, as will the temperature of complete melt formation. However, if reduction of the Cr₂O₃ and iron-oxide components of the spinel in solution in the slag is taking place rapidly, the behaviour of the slag will approximate closely to the above system, which contains Al₂O₃ only.

By use of the phase diagram, it is possible to calculate, to a reasonable degree of accuracy, the liquid content of the slags at any temperature. The cordierite and anorthite of all three slags are present as melt at 1340°C. Where the liquid composition leaves the valley line to join the hatched line, all the silica is present in the liquid, and by a geometric construction it is possible to estimate the amount of spinel in solution at this temperature, thus calculating the total liquid content of slags 1, 2, and 3 at 1675°C, 1575°C, and 1700°C respectively. Liquid contents at the different temperatures are given below:

	Slag 1	Slag 2	Slag 3
(a) Liquid present at 1340°C (%)	21	37	19
(b) Liquid present at junction of valley line and hatched line (%)	81 (1675°C)	91 (1575°C)	92 (1700°C)
(c) Spinel taken into solution between 1340°C and valley line temperature (%)	20	N.D.	23
(d) Spinel taken into solution between valley line temperature and temperature of complete melting (%)	19	N.D.	8
(e) Temperature of complete melt (°C)	1830	1750	1775

Because of the fairly regular spacing between isotherms, the amount of liquid varies almost linearly with temperature, and estimates can be made of the liquid contents and the amount of spinel in solution at any intermediate temperatures.

The presence of the larger amount of cordierite in slag 2 requires complete details of the quaternary system for an accurate determination of the liquid contents and spinel solubilities; so these figures are not given in the above table. If, in practice, reduction of the solid chrome spinel in the slag is taking place, it appears to be important that slag composition and temperature are adjusted in such a way that any MgO·Al₂O₃ spinel formed in the reaction is rapidly dissolved, i.e., no solid reaction rims are formed round the chromium-ore particles. It also appears important that, for good slag workability, the slag composition and slag volume should be adjusted so that all the alumina and magnesia from the original chromium ore are taken

completely into solution when complete reduction has been achieved. If all the spinel is not in solution, primary crystals will be present, which will increase the slag viscosity and may cause problems by settling out in, for example, the taphole area. To achieve optimum spinel solubility, the primary spinel field should be avoided and slag composition should be adjusted to be as close as possible to the valley line *bd* in Figure 12.

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DISCUSSION

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The mechanism of chromite dissolution is interesting. This may explain why additions of CaO are beneficial in decreasing chromium losses in the slag. It appears that CaO additions will either lower the melting-point of the spinel phase or shift the primary phase.

Dr Hayhurst:

Looking at the phase diagram, I would certainly agree that one of the obvious approaches is to increase the lime content. This increases the anorthite content, and I would expect and am very pleased to hear that it is advantageous

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