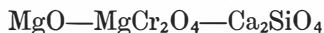


Původní práce

PHASE EQUILIBRIA IN THE SYSTEM



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The approximative position of the ternary eutectic point and approximative temperature of the solidus in the system MgO—MgCr₂O₄—Ca₂SiO₄ were determined by a geometric construction made on the basis of linear and planar shrinkage of samples in the course of heating. By quenching method and by subsequent phase analysis the composition of eutecticum was found to be 78.3 % Ca₂SiO₄, 16.6 % MgCr₂O₄ and 5.1 % MgO and the solidus temperature of 1640 ± 5 °C was found. By measurements of the planar distribution of atoms with the electron microprobe analyzer JXA-5 the atoms Mg and Cr were found in dicalciumsilicate, Ca and Cr in periclase and Ca atoms in picrchromite at temperatures from 1630 to 1740 °C.

INTRODUCTION

The construction of the phase diagram MgO(M)—MgCr₂O₄(MCr)—Ca₂SiO₄(C₂S) contributes, after the phase relations in the systems Ca₃MgSi₂O₈—MCr [1] and MCr—C₂S [2] have been established in our previous works, to the elucidation of phase relations in the quaternary system MgO—CaO—SO₂—Cr₂O₃ at high temperatures. The investigation of phase equilibria in the system M—MCr—C₂S was performed on the basis of known positions and temperatures of eutectic points of the individual binary systems. In the system M—MCr the position of the eutectic point is given by the composition of approx. 80 % M and 20 % MCr and by the solidus temperature approaching 2350 °C [3], in the system MCr—C₂S by the composition 21.5 % MCr and 78.5 % C₂S, temperature of 1660 °C [2] and in the system M—C₂S by the composition 13.5 % M and 86.5 % C₂S and by temperature 1800 °C [4]

EXPERIMENTAL

Determination of regions wherein the phases coexist at high temperatures was performed with the aid of the quenching method, using for this purpose data obtained with the heating microscope Leitz; the latter data gave us approximative information on the composition of eutecticum and on the solidus temperature. In the system M—MCr—C₂S two sections (Fig. 1) were chosen, MCr—C (the composition of the mixture C: 20 % M, 80 % C₂S) and A—B (the composition of A: 95 % C₂S, 5 % M and B: 40 % MCr, 60 % C₂S). With the aid of the centre of gravity principle it may be easily proved that, in the case of the section MCr—C and A—B, the maximal amounts of liquid phase at the solidus temperature and maximal enthalpy

will occur in mixtures from which, up to the solidus temperature, only one solid phase crystallizes (mixtures corresponding to points 1 and 2 in Fig. 1). That means that mixtures corresponding to the points 1 and 2 will, at temperatures slightly higher than the solidus temperature (by 5–10 °C), contain maximal quantity of liquid phase and consequently must display greatest linear shrinkage. For measurements with the heating microscope samples containing 10, 15, 20, 25 % MCr and 90, 85, 80 and 75 % C, respectively, and mixtures with 50, 60, 65, 70 and 80 % A and 50, 40, 35, 30, and 20 % B, respectively, were prepared. Measurements of linear shrinkage were first performed by dynamic method, by recording the shape of the samples at increasing temperature. The mixtures were then heated for 30 minutes at the solidus temperature, as this was determined by the dynamic method which is, however, slightly higher than the actual solidus temperature [1], and the shapes of the samples were photographically recorded.

By a geometric construction the area in which the ternary eutectic point would most probably lie was determined and the quenching measurements concentrated on this area only.

The starting mixtures within the concentration triangle M—MCr—C₂S were prepared from pure minerals MCr and C₂S and from the heavy MgO (Merck analytical-reagent grade). From the homogenized mixture cylinders 3 mm high and 3 mm in diameter were pressed by pressure of approximately 800 kp/cm². The cylinders were enclosed in a Pt foil, heated in air for 2–4 hours at temperatures ranging from 1630 to 1740 °C and subsequently quenched by allowing them to fall from the heating zone of the furnace into a copper block. The furnace temperature was measured by an optical pyrometer. The areas of the coexistence of individual phases were determined by mineralogical evaluation of the polished sections and the formation of solid solutions was observed with the aid of the electron microanalyzer JXA-5.

A detailed description of the preparation and of the evaluation of quenched samples as well as the application of the heating microscope for this purpose were reported in our previous works [1, 2].

RESULTS

1. By measurements of the linear shrinkage with the heating microscope the approximative value of the solidus temperature was found to be 1640–1650 °C. For these measurements mixtures lying on the join MCr—C were used.

2. By measurements of linear and planar shrinkage of samples prepared from mixtures corresponding to the joins MCr—C and A—B, while the samples were heated at constant temperature of 1650 ± 2 °C, for 30 minutes, the maximal values for linear and planar shrinkage were found to pertain to the compositions: 15–20 % MCr and 85–80 % C, point 1, Fig. 1 and 65 % A and 35 % B, point 2, Fig. 1. By a geometric construction (Fig. 1) based on the known positions of points 1 and 2 and from the composition of binary solid solutions at the temperature 1650 °C, the approximative positions of the ternary eutectic point of the composition 6 % M, 76 % C₂S and 18 % MCr were found.

3. By quenching method the areas of coexisting phases were determined

with greater precision. On the basis of 64 measurements the phase diagram was constructed (Fig. 2) according to which the solidus temperature is 1640 ± 5 °C and the composition of the eutecticum 5.1 M, 16.6 MCr and 78.3 % C_2S . The measured isotherms are designated by full, the assumed isotherms by dashed lines. The phase boundaries of the coexisting picrochromite, dicalciumsilicate and periclase with the melt are shown on the microphotographs, Fig. 3, 4, 5 and 6 (these correspond to points 1, 2, 3 and 4 in Table I).

Results of phase analysis of 64 samples which were heated to temperatures ranging from 1630 to 1740 °C are listed in Table I.

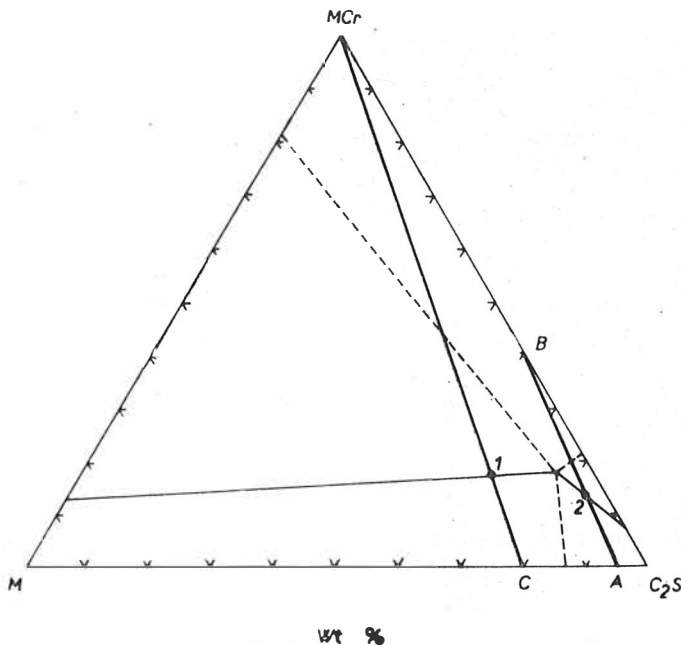


Fig. 1. Sections $MgCr_2O_4 - 20\% MgO, 80\% Ca_2SiO_4$ (MCr—C) and $5\% MgO - 40\% MgCr_2O_4, 60\% Ca_2SiO_4$ (A—B). Geometric construction of the approximative position of the ternary eutectic point in the system $MgO-MgCr_2O_4-Ca_2SiO_4$.

4. By means of the electron microanalyzer the presence of Ca in picrochromite grains, of Cr and Mg in dicalciumsilicate and of Cr and Ca in MgO was proved unambiguously. Further the presence of Si in picrochromite and periclase grains was examined. In this case, however, neither the planar distribution, nor the point analysis gave an unambiguous and satisfactory answer as to the presence of Si in the above grains. Upon comparison of the number of pulses in the point analysis of pure copper with those of periclase it was found that the number of pulses in minerals is always higher (325 imp/10 s in Cu, 504 imp/10 s in picrochromite, 472 imp/10 s in periclase). This difference, however, is not a perfect proof for the presence silicon in the core of the grains.

DISCUSSION

For the geometric construction of the eutectic point the composition of binary solid solutions at a certain temperature was taken, in spite of the fact that beyond any doubt two kinds of atoms (Mg, Cr; Cr, Ca) enter into the structure of dicalciumsilicate and periclase and consequently, these are ternary and not binary solid solutions whose composition in dependence on temperature was not investigated. Generally, the character of the determination of the eutectic point on the basis of linear and planar shrinkage may be regarded as an approach to the solution of this problem and in this sense this inaccuracy is acceptable.

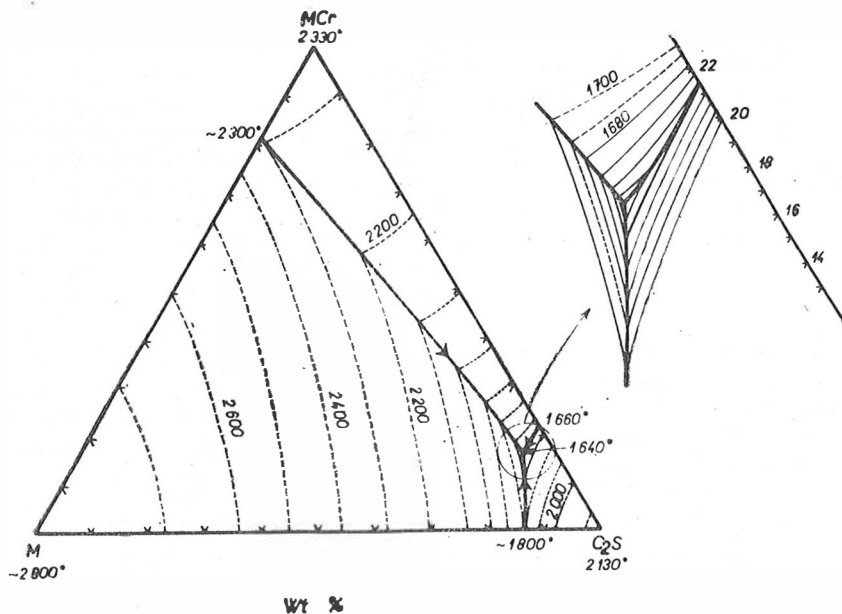


Fig. 2. Phase diagram of the system $\text{MgO—MgCr}_2\text{O}_4\text{—Ca}_2\text{SiO}_4$.

The pressed specimens were inserted into tubes from a Pt foil whose ends were then firmly closed. From samples which contained a greater portion of liquid phase a leakage of this liquid from the Pt wrapping was observed. This may be explained by the action of capillary forces and by the untightness of the wrapping. Since the melt wetted the platinum, the liquid was exhausted at the outer side of the wrapping till an equilibrium was established. As a consequence of this process, in some cases a smaller portion of liquid phase was observed in the polished sections than it actually should be. The quality of the phase analysis is by no means inhibited by this fact, on the contrary, since a part of the liquid phase, which passes entirely into the melt is exhausted, the presence of the primary crystalline phase is stressed.

Melford found that, upon heating MgO with dicalciumsilicate a selective solid solution was formed and the presence of a certain amount of SiO_2 [5] could be proved. These data are in overall agreement with our results, though

Phase Equilibria in the System $MgO-MgCr_2O_4-Ca_2SiO_4$

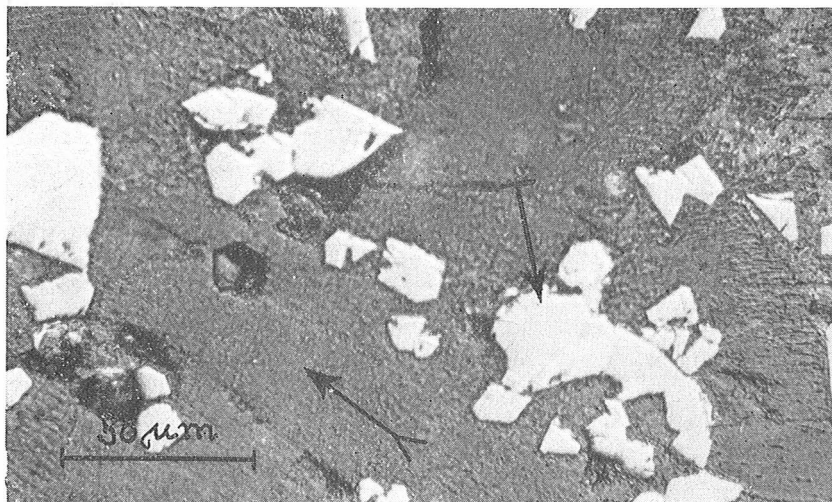


Fig. 3. Micrograph of sample corresponding to the point 1 in Table I.

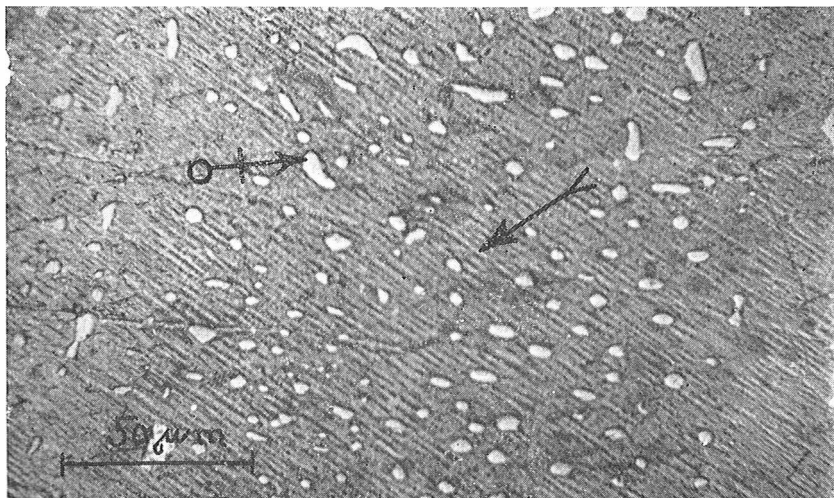


Fig. 4. Micrograph of sample corresponding to the point 2 in Table I.

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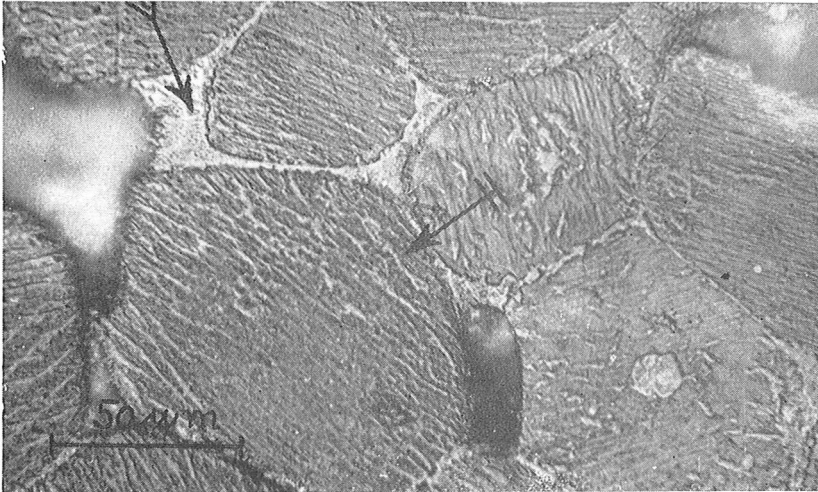


Fig. 5. Micrograph of sample corresponding to the point 3 in Table I.

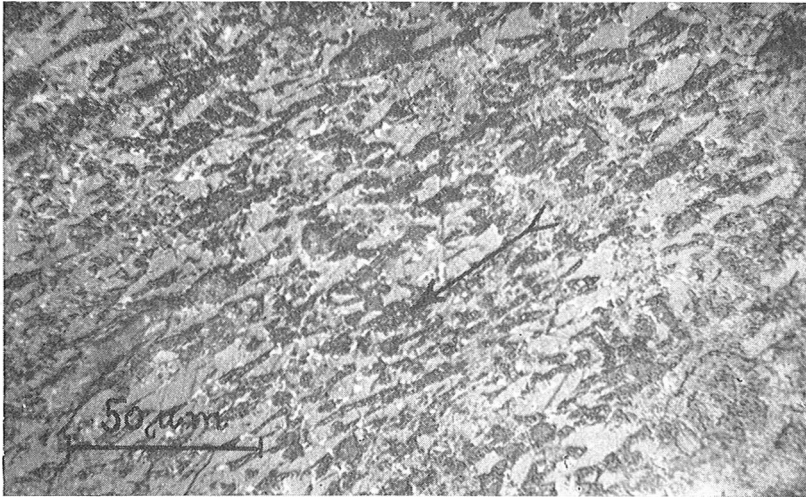


Fig. 6. Micrograph of sample corresponding to the point 4 in Table I.

$\Upsilon = L$; $\Downarrow = MCr$; $\circ = M$; $\bar{\Upsilon} = C_2S$.

Phase Equilibria in the System $MgO-MgCr_2O_4-Ca_2SiO_4$

Table I

Point	Composition wt%			Temp. [°C]	Coexisting Phases	Composition wt%			Temp. [°C]	Coexisting Phases	Point
	MgO	MgCr	C ₂ S			MgO	MgCr	C ₂ S			
1	6	19	75	1720	L	5	17	78	1630	M + C ₂ S + MgCr	2
			77		L					L	
	5	19	76	1710	M + MgCr + L	4	17	79	1700	L	3
			77	M + MgCr + L + (C ₂ S)	3	17	80	1660	C ₂ S + L		
	4	19	77	1710	L	7	15	78	1700	MgCr + L	2
				1690	M + MgCr + L				1700	M + L	
	3	19	78	1680	MgCr + L	5	15	80	1680	M + C ₂ S + L	3
				1670	MgCr + L				1720	L	
	2	19	79	1650	MgCr + C ₂ S + L	18	10	72	1700	C ₂ S + L	3
				1660	MgCr + L				1680	C ₂ S + L + (MgCr)	
	6	17	77	1650	L + (C ₂ S)	17	15	68	1650	M + MgCr + C ₂ S + L	3
				1660	C ₂ S + L + (MgCr)				1640	M + L	
4	5	17	78	1700	L	3,25	14	82,75	1740	C ₂ S + MgCr + L	3
			77	M + L	1700				M + L		
	5	17	78	1690	M + MgCr + L	18	20	64	1740	M + L	3
				1680	M + MgCr + L				1700	M + L	
	6	17	77	1660	M + MgCr + L	15	25	60	1740	M + MgCr + L	3
				1650	M + MgCr + L + (C ₂ S)				1700	M + MgCr + L	
	5	17	78	1640	M + MgCr + C ₂ S + L	2,5	20	77,5	1660	M + MgCr + L	3
				1630	M + MgCr + C ₂ S				1660	MgCr + L	
	5	17	78	1660	L	3,5	12	84,5	1670	C ₂ S + L	3
				1650	L + (MgCr)				1660	C ₂ S + L	
	5	17	78	1640	C ₂ S + MgCr + L	4	8	88	1660	C ₂ S + L	3
				1630	C ₂ S + MgCr + L				1660	C ₂ S + L	

Temperature was kept at 1740—1700 °C for 2 hours, at 1690—1660 for 3 hours and at 1650—1630 for 4 hours

the presence of Si atoms in MgO could not be proved unambiguously, perhaps also because the duration of the heating was too short. On the polished sections only picrochromite, dicalciumsilicate, periclase and the melt were observed at temperatures higher than 1640 °C and below this temperature only picrochromite, periclase and dicalciumsilicate were detected. On the basis of these measurements it was not possible to decide on the character of the binding of the superfluous SiO₂. With regard to the solubility of MgO in dicalciumsilicate the exchange reaction between Ca²⁺ and Mg²⁺ can be assumed only to a very limited extent.

Whereas it could be proved on the basis of planar distribution of atoms that two extraneous atoms enter into the structure of periclase and dicalciumsilicate grains, i.e. that ternary solid solutions are formed, in case of picrochromite an additional and very careful quantitative analysis should be performed.

CONCLUSIONS

Samples treated by quenching over the temperature range from 1630 to 1740 °C were submitted to microscopic phase analysis. From the results of phase analysis in dependence on temperature the composition of eutecticum was found to be 78.3 % C₂S, 16.6 % MCr and 5.1 % M and the solidus temperature of 1640 ± 5 °C was established. With the aid of electron microanalyzer the presence of periclase and dicalciumsilicate in the form of ternary solid solutions could be proved, from among the extraneous atoms only calcium was detected in the grains of picrochromite.

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FÁZOVÉ ROVNOVÁHY V SYSTÉMU MgO—MgCr₂O₄—Ca₂SiO₄

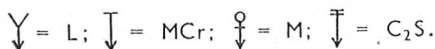
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Na základe merania lineárneho a plošného zmrštenia vzorkov pri záhreve vymedzila sa geometrickou konštrukciou približná poloha ternárneho, eutektického bodu a približná teplota solidus sústavy MgO—MgCr₂O₄—Ca₂SiO₄. Statickou metódou náhleho ochladenia a nasledujúcou fázovou analýzou stanovilo sa zloženie eutektika 78,3 % Ca₂SiO₄, 16,6 % MgCr₂O₄ a 5,1 % MgO a teplota solidus 1640 ± 5 °C. Meraním plošného rozloženia atomov vzorkov pomocou elektrónovej mikrosondy JXA-5 sa zistila prítomnosť Mg a Cr atomov v dicalciumsilikáte, prítomnosť atomov Ca a Cr v periklase a prítomnosť atomov Ca v zrnách picrochromitu v rozsahu teplôt 1630—1740 °C. Prítomnosť atomov Si sa nedokázala jednoznačne ani v zrnách picrochromitu ani periklasu. Nakoľko pod teplotou 1640 °C nebola zistená prítomnosť kvapalnej fáze, nebolo možné rozhodnúť, na základe vykonaných meraní o spôsobe väzby prebytočného SiO₂. S ohľadom na rozpustnosť MgO v Ca₂SiO₄ je možné predpokladať výmennú reakciu medzi Ca²⁺ a Mg²⁺ ve veľmi obmedzenom rozsahu.

Phase Equilibria in the System $MgO-MgCr_2O_4-Ca_2SiO_4$

- Obr. 1. Znážornenie rezov $MgCr_2O_4$ — 20 % MgO , 80 % Ca_2SiO_4 (MCr—C) a 95 % Ca_2SiO_4 , 5 % MgO — 40 % $MgCr_2O_4$ 60 % Ca_2SiO_4 (A—B). Geometrická konštrukcia približnej polohy ternárneho eutektického bodu v sústave $MgO-MgCr_2O_4-Ca_2SiO_4$.
- Obr. 2. Fázový diagram sústavy $MgO-MgCr_2O_4-Ca_2SiO_4$.
- Obr. 3. Mikrofotografie vzorku odpovedajúce bodu 1 v tab. I.
- Obr. 4. Mikrofotografie vzorku odpovedajúce bodu 2 v tab. I.
- Obr. 5. Mikrofotografie vzorku odpovedajúce bodu 3 v tab. I.
- Obr. 6. Mikrofotografie vzorku odpovedajúce bodu 4 v tab. I.



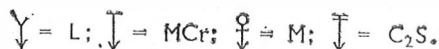
ФАЗОВОЕ РАВНОВЕСИЕ В СИСТЕМЕ $MgO-MgCr_2O_4-Ca_2SiO_4$

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На основании измерения линейной и поверхностной усадки проб при нагреве было при помощи геометрической конструкции установлено приблизительное положение тернарной эвтектической точки и приблизительная температура солидуса системы $MgO-MgCr_2O_4-Ca_2SiO_4$. При помощи статического метода резкого охлаждения и последующего фазового анализа установили состав эвтектика 78,3 % Ca_2SiO_4 , 16,6 % $MgCr_2O_4$, 16,6 % $MgCr_2O_4$ и 5,1 MgO и температура солидуса 1640 ± 5 °C. Путем измерения плоскостного расположения атомов проб при помощи электронного микронзонда JXA-5 установили присутствие Mg и Cr атомов в дикальцийсиликате, присутствие атомов Ca и Sr в периклазе и присутствие атомов Ca в зернах микрохромита в пределах температур 1630—1740 °C. Присутствие атомов Si не удалось однозначно доказать ни в зернах микрохромита, ни периклаза. Так как при температуре 1640 °C не было установлено присутствие жидкой фазы, нельзя было на основании проведенных измерений решить вопрос способа связи избыточной SiO_2 . Имея в виду растворимость MgO в Ca_2SiO_4 можно предполагать реакцию обмена между Ca^{2+} и Mg^{2+} в весьма ограниченном размере.

- Рис. 1. Изображение разрезов $MgCr_2O_4$ — 20 % MgO , 80 % Ca_2SiO_4 (MCr—C) и 95 % Ca_2SiO_4 , 5 % MgO — 40 % $MgCr_2O_4$ 60 % Ca_2SiO_4 (A—B). Геометрическая конструкция приблизительного положения эвтектической точки в системе $MgO-MgCr_2O_4-Ca_2SiO_4$.
- Рис. 2. Фазовая диаграмма системы $MgO-MgCr_2O_4-Ca_2SiO_4$.
- Рис. 3. Микрофотосъемка пробы, соответствующей точке 1 в таблице I.
- Рис. 4. Микрофотосъемка пробы, соответствующей точке 2 в таблице I.
- Рис. 5. Микрофотосъемка пробы, соответствующей точке 3 в таблице I.
- Рис. 6. Микрофотосъемка пробы, соответствующей точке 4 в таблице I.



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