Experimental Establishment of the CaAl_2O_4 – MgO and CaAl_4O_7 – MgO Isoplethal Sections within the Al_2O_3 – MgO – CaO Ternary System

Teresa Durán, Sara Serena, Pilar Pena, Ángel Caballero, Salvador De Aza,** and Antonio H. De Aza†

Instituto de Cerámica y Vidrio (CSIC), Cantoblanco, 28049 Madrid, Spain

The isoplethal sections CaAl_2O_4 – MgO and CaAl_4O_7 – MgO of the Al_2O_3 – MgO – CaO ternary system have been experimentally established at 1 bar total pressure and air of normal humidity. The sections obtained provide new data and information that are in disagreement with thermodynamic evaluations and optimizations of the Al_2O_3 – MgO – CaO ternary system published to date. These differences arise mainly from the inclusion, or exclusion, of the binary compound $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, mayenite, as a stable phase in the reported studies of the system. The presence or absence of this compound within the system has an important impact on the solid state and melting relationships of the whole ternary system. The present study confirms the solid-state compatibility CaAl_2O_4 – MgO and CaAl_2O_4 – MgO – MgAl_2O_4 up to $1372^\circ \pm 2^\circ\text{C}$, the peritectic melting point of the later mentioned subsystem.

I. Introduction

THE ternary system Al_2O_3 – MgO – CaO is remarkably important in the field of geology, metallurgy, and ceramic materials, specifically in refractories.^{1–3} Making use of the thermodynamic information provided by this system, different kind of materials can be designed. Besides materials for nuclear waste storage⁴ or catalysis applications,⁵ there are a wide range of refractory materials that can be developed. Some outstanding examples are: synthetic slags for secondary steel refining,⁶ different types of new refractory cements, as spinel-containing cements,⁷ and improved refractory concretes.^{8,9} In this connection, the increasing importance of steel ladles in modern steel-making technology, and the ever-increasing concern with steel cleanliness and the efficiency of steel desulfurization achieved in secondary steelmaking, has led to an increasing demand for alumina–spinel, alumina–magnesia, and alumina–spinel–magnesia castable compositions due to their better corrosion resistance.^{10–18} Thus, the optimization of the scientific knowledge about the ternary system Al_2O_3 – MgO – CaO is not only vital to understanding the behavior of these materials; it is also essential for manufacturing the materials reproducibly, effectively, and economically.

A recent and complete literature review of the data available about the Al_2O_3 – MgO – CaO ternary system can be found elsewhere.¹⁹ However, it is worth pointing out that the most recent studies have shown significant disagreements concerning solid-state compatibility and melting relationships within the mentioned ternary system.^{19–22} These differences arise mainly from the inclusion, or exclusion, of the binary compound

$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, mayenite,^{23,24} namely C_{12}A_7 in short,[‡] as a stable phase in the reported studies of the system. The presence or absence of this compound within the system has an important impact on the solid-state and melting relationships of the whole ternary system changing most of these relationships.

Concerning this point, Majumdar²⁵ included this phase in his study of the ternary system, but the same group only 1 year later,²⁶ based on a thorough study of the $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ phase, concluded that it is not stable in the strictly anhydrous Al_2O_3 – CaO system but is only stabilized by the presence of moisture. Later on, Kohatsu and Brindley²⁷ obtained this phase in dry atmospheres, although they noted that its formation kinetics were more favorable in moist atmospheres,²⁸ and lastly Srikanth *et al.*²⁹ claimed that it is a stable phase in the Al_2O_3 – CaO system. In fact, mayenite is readily obtained in air of normal humidity and exhibits a reversible water sorption–desorption.³⁰ Nowadays $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is a well-known component of cement clinkers but questions remain over the exact stoichiometry of the material.³¹ Therefore, a conclusive study of the $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ phase would be most welcome.

Because $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is a stable phase in normal-humidity air and water is present in many technological and geological processes, the compound $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ should be considered to be a stable phase under ambient conditions. At this point, it is important to point out that the most recent thermodynamic critical evaluations and modeling of the diagram^{19,20} omitted this phase and, under this assumption, give some solid-state compatibility and melting relationships within the mentioned ternary system that are not in agreement with previous experimental results^{21,22,25,32,33} at 1 bar total pressure and in air of normal humidity, conditions under which many technological processes take place.

To summarize, there is a lack of understanding of the *in situ* formation spinel materials, and this is even more conspicuous in the case of magnesia castables.¹⁰ The correct design, development, and understanding of these materials require the exact knowledge of the above-mentioned solid-state compatibility and melting relationships within the Al_2O_3 – MgO – CaO system. In the present investigation, the experimental determination of the isoplethal sections MgO – CaAl_2O_4 and MgO – CaAl_4O_7 has been considered necessary in order to clarify this issue.

II. Experimental Procedure

The starting materials used in this investigation were: alumina (Al_2O_3) of high-purity CT-3000-SG (Alcoa, Pittsburgh, PA), analytical-grade calcite, CaCO_3 (Merck, Darmstadt, Germany), and pure periclase, MgO (Merck).

(1) Synthesis of Calcium Aluminates

Before the experimental determination of the isoplethal sections, it was necessary to synthesize both calcium aluminates involved in the study: CA, and CA_2 .

The desired proportions of the starting materials (Al_2O_3 and CaCO_3) were weighed out and a 50 wt% solids suspension was prepared in isopropyl alcohol. To obtain a homogeneous and high energetic milled batch, the suspension of the mixture was

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**Fellow, American Ceramic Society.

†Author to whom correspondence should be addressed. e-mail: aaza@icv.csic.es

‡For simplicity, in figures and tables of this paper, cited compounds are described by abbreviated formulas: C = CaO , M = MgO , and A = Al_2O_3 (i.e. $\text{CaAl}_2\text{O}_4 = \text{CaO} \cdot \text{Al}_2\text{O}_3 = \text{CA}$; $\text{CaAl}_4\text{O}_7 = \text{CaO} \cdot 2\text{Al}_2\text{O}_3 = \text{CA}_2$; $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33} = 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 = \text{C}_{12}\text{A}_7$; $\text{MgAl}_2\text{O}_4 = \text{MgO} \cdot \text{Al}_2\text{O}_3 = \text{MA}$).

wet ground in a laboratory closed-chamber attrition mill using high-purity 3 mm Y_2O_3 -stabilized ZrO_2 balls (Tosho Europe B.V., Amsterdam Z.O., the Netherlands) as grinding media. The batches were milled for 6 h, and the average particle size of the final batches, measured by laser diffraction (Model LS 130, Coulter Corp., Miami, FL), was around 2–3 μm . After the milling process, the mixtures were dried and burned at 950°C for 2 h to remove the CO_2 . Then, this powder was sieved to <100 μm and cold isostatically pressed at 200 MPa to produce green compacts ~100 mm in length and ~10 mm in diameter.

These compacts were heat treated at 1380°C for the CaAl_2O_4 batch and 1550°C for the one of CaAl_4O_7 , with a heating and cooling rate of 5°C/min. The reaction-sintering temperatures were selected bearing in mind the information provided by the $\text{CaO-Al}_2\text{O}_3$ phase equilibria diagram evaluated and reported by Hallstedt³⁴ and reevaluated by Mao *et al.*³⁵ The materials obtained were ground in a tungsten carbide rings mill then cold isostatically pressed and reheated again. This procedure was repeated once to obtain an X-ray diffraction (XRD) pattern (Bruker-Siemens D5000, Karlsruhe, Germany) that showed the presence of either CaAl_2O_4 or CaAl_4O_7 as the only present phase (Fig. 1). The bulk density of the obtained CaAl_2O_4 and CaAl_4O_7 compact cylinders, measured by the Archimedes method, was 95.4% and 95.5%, respectively. These synthetic calcium aluminates were also examined by a field emission scanning electron microscope FE-SEM, (Hitachi-S4700, Tokyo, Japan), fitted with X-ray energy-dispersive spectrometry, EDS (Noran System Six—Thermo Electron Corporation, Waltham, MA). Figure 1 also shows the microstructure of both synthesized raw materials. The semiquantitative microanalyses performed on polished and thermally etched surfaces of the samples with the

Table I. Selected Compositions

Sample designation	Composition (wt%)		
	CaAl_2O_4	CaAl_4O_7	MgO
60CA	60.000	—	40.000
80CA	80.000	—	20.000
90CA	90.000	—	10.000
98CA	98.000	—	2.000
70CA ₂	—	70.000	30.000
84CA ₂	—	84.000	16.000
98CA ₂	—	98.000	2.000

All values are displayed up to the last certain figure.

EDS microprobe analyzer (Oyster Bay, NY) were (in wt%): 36.8 ± 1.2 CaO, and 63.2 ± 1.1 Al_2O_3 for CaAl_2O_4 and 22.7 ± 1.3 CaO, 77.3 ± 1.0 Al_2O_3 for CaAl_4O_7 . Keeping in mind the precision of the method and the given standard deviation for five microanalyses, both materials are almost stoichiometric for experimental purpose.

These synthetic calcium aluminates were ground in the above-mentioned tungsten carbide rings mill to obtain fine powders of 11 and 13 μm mean particle size and 0.5 and 0.3 m^2/g specific surface areas (N_2 adsorption BET method, Monosorb Surface Area Analyser MS-13, Quantachrome Co., Hook, UK), respectively. The real densities measured by helium pycnometry (Multipycnometer, Quantachrome Co.) were 2.88 for CaAl_2O_4 and 2.89 g/cm^3 for CaAl_4O_7 .

(2) Experimental Study of the Isoplethal Sections

Seven selected compositions were prepared and studied (Table I) at different temperatures to establish the solid-state compatibility and melting relationships in the CaAl_2O_4 -MgO and CaAl_4O_7 -MgO isoplethal sections of the Al_2O_3 -MgO-CaO system. Calculated batches were weighed from dry powders, at 110°C/24 h, of the above-mentioned raw materials, except MgO, which was calcined at 950°C. The compositions were mixed in acetone and dried in air. This procedure was repeated three times to ensure homogeneity. Samples were uniaxially pressed at 200 MPa into a cylindrical shape in a die (5 mm in diameter and 5 mm long).

Samples were loaded into small platinum-foil crucibles and fired in air at the selected temperatures in a high-temperature furnace (up to 1800°C in air) with Super-Kanthal heating elements (Switzerland), which was equipped with an electronic temperature controller with an accuracy of $\pm 1^\circ\text{C}$ (902–904 series, Invensys Eurotherm, West Sussex BN13 3PL). The platinum crucibles, with the samples inside, were suspended in the hot zone of the electrical furnace by a platinum wire. A calibrated Pt/6Rh–Pt/30Rh thermocouple, with its tip almost in contact with the samples, was attached to the crucibles. The time period that was required to attain equilibrium was between 10 and 35 h. After heat treatment, the samples were cold air quenched. Sometimes, the samples were reground after quenching and then pressed and fired again, to ascertain the attainment of equilibrium.

After quenching, the specimens were removed from the platinum crucibles and diamond-machined fragments from the sample blocks were mounted in an epoxy resin. Then, the mounted samples were polished using different grades of diamond up to 1 μm . A cerium suspension was used for finishing when it was necessary.

The first phase analysis of the equilibrated specimens was performed using reflected-light microscopy (Model HP 1, Carl Zeiss, Oberkochen and Jena GmbH, Germany) on the polished and chemically etched surfaces of the samples. Different etching solutions were used to distinguish between phases. For instance, CaAl_2O_4 , when etched with steam for 15–30 s, yielded a blue or

Fig. 1. The upper part of the figure shows the X-ray diffraction (XRD) pattern of the synthesized powders. Patterns reveal the presence of either CA or CA_2 as the only present phase (23-1036 and 23-1037 PDF files, respectively). The lower part of the figure shows field emission scanning electron microscope (FE-SEM) images of the microstructure of both synthesized raw materials before they were ground. The polished and gold-coated surfaces were thermally etched at 1240° and 1395°C, respectively, for 2 h to highlight the grain boundaries.

Fig. 2. CALPHAD⁴⁰ calculated isoplethal sections from thermodynamic functions proposed by Hallstedt.^{20,34,41} (a) CaAl_2O_4 - MgO and (b) CaAl_4O_7 - MgO . Calculations carried out using the thermodynamic parameters reported by Jung *et al.*¹⁹ give isoplethal sections that are qualitatively the same, but in which some temperatures and compositions differ from those of Hallstedt.^{20,34,41} See text for details.

Table II. Phases Identified in Equilibrium in the Selected Compositions of the Isoplethal Section CaAl_2O_4 – MgO

Sample designation	Temperature (°C)/time (h) [†]				
	1340° ± 1°/16+16	1402° ± 1°/11+12	1559° ± 1°/13+14	1658° ± 1°/10+10	1733° ± 1°/10
60CA	MgO+CA	MgO+MA+L	—	MgO+MA+L	MgO+L
80CA	MgO+CA	MgO+MA+L	MgO+MA+L	L	L
90CA	MgO+CA	CA+MA+L	MA+L	L	—
98CA	MgO+CA	CA+MA+L	CA+L	L	L

[†]Sometimes it was necessary to regrind the samples to ascertain the attainment of equilibrium. This intermediate regrind is indicated by a “+” symbol. The equilibrium conditions were evaluated by reflected-light microscopy and FE-SEM. Phases were identified by XRD and semi-quantitative EDS microprobe analyzer. CA, CaAl_2O_4 ; MA, MgAl_2O_4 ; L, liquid phase at the indicated temperature; FE-SEM, field emission scanning electron microscope; XRD, X-ray diffraction; EDS, energy-dispersive spectrometry.

brown color, depending on the crystal orientation. However, CaAl_4O_7 , when etched with HF (5 vol%) for 20–30 s, yielded a bluish-pink color.

The microstructures of the samples were also studied on polished and gold-coated surfaces via the above-mentioned field FE-SEM. Individual phases were analyzed using the Noran System Six—Thermo Electron Corporation EDS mentioned previously.

Qualitative phase analysis was performed using XRD. XRD patterns were recorded on the previously mentioned Bruker-Siemens D5000 automated diffractometer, using $\text{CuK}\alpha_{1,2}$

radiation (1.5418 Å) and a secondary curved graphite monochromator. Data were collected in the Bragg–Brentano ($\theta/2\theta$) vertical geometry (flat reflection mode) between 2° and 70° (2θ) in 0.05° steps, counting for 1.5 s per step. Samples were rotated at 15 rpm during acquisition of patterns in order to improve averaging. A system of primary Soller foils between the X-ray tube and the fixed aperture slit was used. One scattered radiation slit of 1 mm was placed after the sample, followed by a system of secondary Soller slits and a detector slit of 0.1 mm. The X-ray tube was operated at 40 kV at 30 mA.

Fig. 3. Evolution of the selected compositions with temperature, followed by X-ray diffraction (XRD) after quenching. It is worth mentioning that XRD patterns sometimes show devitrified phases during quenching. The use of microscopy techniques allows to elucidate the phases in equilibrium.

Fig. 4. Typical field emission scanning electron microscope (FE-SEM) images of the microstructures, within different fields of crystallization, of samples after quenching from various annealing temperatures. The different phases were identified using the mentioned FE-SEM fitted with EDS. (a) 60CA at $1658^\circ \pm 1^\circ\text{C}$; (b) 60CA at $1733^\circ \pm 1^\circ\text{C}$; (c) 90CA at $1402^\circ \pm 1^\circ\text{C}$; (d) 90CA at $1559^\circ \pm 1^\circ\text{C}$; (e) 98CA at $1559^\circ \pm 1^\circ\text{C}$; (f) 98CA at $1733^\circ \pm 1^\circ\text{C}$.

III. Results and Discussion

(1) Thermodynamic Calculations

The main differences between the thermodynamic assessments reported for the Al_2O_3 - MgO - CaO ternary system^{19,20} are related to the models used for describing the liquid and solid phases, and the inclusion of different phases.

In this way, in the optimization reported by Hallstedt,²⁰ the liquid phase was described by the two-sublattice model for ionic liquids,³⁶ while spinel (only considering MgO as a solid solution) and MgO and CaO (with different solid solutions) were described as solution phases using two-sublattice models.³⁷ All the calcium aluminates phases, and also α - Al_2O_3 , were treated as stoichiometric phases. Only $\text{Ca}_3\text{MgAl}_4\text{O}_{10}$, $\text{C}_3\text{A}_2\text{M}$ in short, was included as a ternary phase in the system and its Gibbs free energy was evaluated relative to the pure oxide CaO , MgO , and Al_2O_3 .

On the other hand, more recent models were used in the optimization reported by Jung *et al.*¹⁹ In this assessment, the modified quasichemical model³⁸ was used to describe the liquid phase while the spinel (only taking into consideration MgO as a solid solution) was described by the two-sublattice compound energy formalism.³⁹ The ternary phases $\text{Ca}_3\text{MgAl}_4\text{O}_{10}$ (mentioned

Fig. 5. Experimental CaAl_2O_4 - MgO isoplethal section of the Al_2O_3 - MgO - CaO ternary system plotted with the results obtained.

above), $\text{CaMg}_2\text{Al}_{16}\text{O}_{27}$ (CA_8M_2 in short), and $\text{Ca}_2\text{Mg}_2\text{Al}_{28}\text{O}_{46}$ ($\text{C}_2\text{A}_{14}\text{M}_2$ in short) were included in the assessment and the corresponding Gibbs-free energy functions were optimized.

To summarize, the calculated projections of the liquidus surface of both thermodynamic assessments of the system mainly differ in the Al_2O_3 corner, due to the inclusion of the ternary phases $\text{CaMg}_2\text{Al}_{16}\text{O}_{27}$ and $\text{Ca}_2\text{Mg}_2\text{Al}_{28}\text{O}_{46}$ in the thermodynamic assessment reported by Jung *et al.*¹⁹ The remaining invariant points resulting from both optimizations are very similar. Here, it is worth reminding that none of the above-mentioned assessments, include the binary compound $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ as a stable phase.

For an easier comparison among the previously published thermodynamic data^{19,20} and the experimental results obtained in the present work, the isoplethal sections CaAl_2O_4 - MgO and CaAl_4O_7 - MgO , of the Al_2O_3 - MgO - CaO , were calculated following the CALPHAD (CALCulation of PHASE Diagrams) methodology⁴⁰ from thermodynamic functions for the system proposed by Hallstedt.^{20,34,41} The thermodynamic calculations were carried out using THERMO-CALC software-databank⁴² version P. Figures 2(a) and (b) show the calculated phase diagrams for both isoplethal sections.

Here it is worth mentioning that calculations carried out using the parameters reported by Jung *et al.*¹⁹ give isoplethal sections that are qualitatively the same, but in which some temperatures and compositions differ significantly from those of Hallstedt.^{20,34,41} For example, the lines shown at 1716° and 1875°C in Figs. 2(a) and (b) are calculated at 1620° and 1810° , respectively, when the parameters of Jung *et al.*¹⁹ are used.

(2) CaAl_2O_4 - MgO Isoplethal Section

Table II shows the selected compositions within the CaAl_2O_4 - MgO isoplethal section with the temperature and time of each thermal treatment, when samples were reground to ascertain the attainment of equilibrium is indicated, and the identified coexisting phases at equilibrium are shown. Figure 3 shows the evolution of these selected compositions with temperature, followed by XRD. Here, it is important to point out that XRD patterns sometimes show devitrified phases during quenching. See for example the pattern recorded for the sample 98CA treated at 1658°C for 20 h (Fig. 3(d)). Therefore, the use of microscopy techniques to elucidate the phases in equilibrium is indispensable. Figure 4 shows typical FE-SEM images of the microstructures, within different fields of crystallization, of samples after quenching from various annealing temperatures. The different phases were identified using FE-SEM fitted with EDS (Table II).

The experimental CaAl_2O_4 - MgO isoplethal section of the Al_2O_3 - MgO - CaO ternary system that was plotted with the results obtained is shown in Fig. 5.

The obtained section provides new information that is in disagreement with the published thermodynamic evaluations and optimizations of the Al_2O_3 - MgO - CaO ternary system.^{19,20}

Fig. 6. Evolution of the selected compositions with temperature, followed by X-ray diffraction (XRD) after quenching. As mentioned previously, XRD patterns sometimes show devitrified phases during quenching. The use of microscopy techniques allows to elucidate the phases in equilibrium.

This isoplethal section shows the existence of the solid-state compatibility $\text{CaAl}_2\text{O}_4\text{--MgO}$ that is nonexistent in the isoplethal section calculated using the data given by Jung *et al.*¹⁹ and Hallstedt²⁰; compare Figs. 2(a) and 5. The present experimental data reveal that these phases are compatible up to $1372^\circ \pm 2^\circ\text{C}$. At this temperature, a liquid phase begins to exist and develop. This temperature and the composition of the P3 denoted point in Fig. 5 correspond to the projection, on this isoplethal section, of the peritectic melting point of the $\text{CaAl}_2\text{O}_4\text{--MgO--MgAl}_2\text{O}_4$ subsystem within the $\text{Al}_2\text{O}_3\text{--MgO--CaO}$ ternary system, located at 52.5% Al_2O_3 , 40.55% CaO , and 6.95% MgO (wt%) according to De Aza *et al.*,^{21,22} see Fig. 9. The remaining isoplethal section, shown in Fig. 5, also differs from the calculated section using the above-mentioned thermodynamic published data^{19,20} in the nonexistence of the solid-state compatibility $\text{MgO--MgAl}_2\text{O}_4\text{--Ca}_3\text{MgAl}_4\text{O}_{10}$ (Fig. 2(a)).

On the other hand, it is worth mentioning that the points denoted as M and N in Fig. 5 confirm the composition and temperature reported by De Aza *et al.*^{21,22} for these points within the $\text{Al}_2\text{O}_3\text{--MgO--CaO}$ ternary system (Fig. 9). That is to say, M ($1695^\circ \pm 10^\circ\text{C}$) lies on the monovariant boundary line that delimits the primary field of crystallization of MgAl_2O_4 and MgO and N ($1480^\circ \pm 10^\circ\text{C}$) on the monovariant boundary line that delimits the primary field of crystallization of MgAl_2O_4 and CaAl_2O_4 within the ternary system.

(3) $\text{CaAl}_4\text{O}_7\text{--MgO}$ Isoplethal Section

Table III shows the selected compositions within the $\text{CaAl}_4\text{O}_7\text{--MgO}$ isoplethal section with the temperature and time of each thermal treatment. To ascertain the attainment of equilibrium, it

was necessary to regrind samples after the first thermal treatment, as indicated in the table. This procedure was repeated twice in the case of some samples. The identified coexisting phases at equilibrium are shown in the table mentioned above. Figure 6 shows the evolution of these selected compositions with temperature, followed by XRD. Figure 7 shows typical FE-SEM microscopy images of the microstructures, within different fields of crystallization, of samples after quenching from various annealing temperatures. The different phases were identified, as in the previous case, using FE-SEM fitted with EDS (Table III).

The established experimental $\text{CaAl}_4\text{O}_7\text{--MgO}$ isoplethal section of the $\text{Al}_2\text{O}_3\text{--MgO--CaO}$ ternary system that was plotted with the results obtained is shown in Fig. 8. Once again, the obtained section provides new information that is in disagreement with the published thermodynamic evaluations and optimizations of the $\text{Al}_2\text{O}_3\text{--MgO--CaO}$ ternary system.^{19,20}

This experimental isoplethal section again confirms the existence of the solid-state compatibility $\text{CaAl}_2\text{O}_4\text{--MgO--MgAl}_2\text{O}_4$ that is nonexistent in the isoplethal section calculated using the data proposed by Jung *et al.*¹⁹ and Hallstedt,²⁰ compare Figs. 2(b) and 8. Once again, the present data reveal that these phases are compatible up to $1372^\circ \pm 2^\circ\text{C}$, which is, as mentioned previously, the temperature of the peritectic melting point of the $\text{CaAl}_2\text{O}_4\text{--MgO--MgAl}_2\text{O}_4$ subsystem (point P3 in Figs. 8 and 9).

The point marked as P4 in Fig. 8 corresponds to the projection on the $\text{CaAl}_4\text{O}_7\text{--MgO}$ isoplethal section of the invariant peritectic point of the $\text{CaAl}_2\text{O}_4\text{--CaAl}_4\text{O}_7\text{--MgAl}_2\text{O}_4$ subsystem within the $\text{Al}_2\text{O}_3\text{--MgO--CaO}$ ternary system that takes place at $1567^\circ \pm 2^\circ\text{C}$ and is located, according to De Aza *et al.*,^{21,22} at 63.2% Al_2O_3 , 33.3% CaO , and 3.50% MgO (wt%); see Fig. 9.

Fig. 7. Typical field emission scanning electron microscope (FE-SEM) images of the microstructures, within different fields of crystallization, of samples after quenching from various annealing temperatures. The different phases were identified using the mentioned FE-SEM fitted with EDS. (a) 70CA₂ at 1477°±1°C; (b) 84CA₂ at 1477°±1°C; (c) 84CA₂ at 1653°±1°C; (d) 98CA₂ at 1653°±1°C; (e) 98CA₂ at 1714°±1°C.

Additionally, it is important to mention that the points denoted as W and X in Fig. 8 confirm the composition and temperature for these points within the Al_2O_3 - MgO - CaO ternary system (Fig. 9). To be precise, W (~1800°C) lies on the monovariant boundary line that delimits the primary field of crystallization of MgAl_2O_4 and MgO and X (1683°±10°C) on the monovariant boundary line that delimits the primary field of crystallization of MgAl_2O_4 and CaAl_2O_4 within the ternary system. Likewise, the broad extension of the primary field of crys-

Fig. 8. Experimental CaAl_4O_7 - MgO isoplethal section of the Al_2O_3 - MgO - CaO ternary system plotted with the results obtained.

tallization of spinel, within the ternary system, is also highlighted (see Fig. 9).

Finally, the remaining isoplethal section indicated in Fig. 8 once again confirms that the solid-state compatibility MgO - MgAl_2O_4 - $\text{Ca}_3\text{MgAl}_4\text{O}_{10}$ does not exist at 1 bar total pressure and air of normal humidity, conditions under which many technological developments and processes take place, and neither exists MgAl_2O_4 - $\text{Ca}_3\text{MgAl}_4\text{O}_{10}$ - CaAl_2O_4 solid-state compatibility.

IV. Conclusions

The following concluding remarks can be drawn:

(1) The isoplethals sections CaAl_2O_4 - MgO and CaAl_4O_7 - MgO of the Al_2O_3 - MgO - CaO ternary system have been experimentally established at 1 bar total pressure and in air of normal humidity. Both sections are real pseudobinary systems.

(2) The obtained sections provide new experimental data and information that is in disagreement with thermodynamic evaluation and optimization of the Al_2O_3 - MgO - CaO ternary system published to date. The main differences can be summarized as follows:

(a) The existence of the solid-state compatibility CaAl_2O_4 - MgO up to 1372°±2°C has been confirmed.
(b) The existence of the solid-state compatibility CaAl_2O_4 - MgO - MgAl_2O_4 has also been proved. These phases are compatible up to 1372°±2°C, the temperature of the peritectic melting point of the mentioned subsystem within the Al_2O_3 - MgO - CaO ternary system.

(3) These differences arise mainly from the exclusion or inclusion of the binary compound $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, Mayenite, as a stable phase in the reported studies of the system. The presence or absence of this compound within the system has an important impact on the solid-state and melting relationships of the whole ternary system changing most of these relationships. Because $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is a stable phase in normal-humidity air and water is present in many technological and geological processes, the compound $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ should be considered to be a stable phase under ambient conditions.

Table III. Phases Identified in Equilibrium in the Selected Compositions of the Isoplethal Section CaAl_4O_7 - MgO

Sample designation	Temperature (°C)/time (h) [†]			
	1340°±1°/16+16	1477°±1°/13+12	1653°±1°/10+12+13	1714°±1°/12
70CA ₂	CA+MgO+MA	MgO+MA+L	MgO+MA+L	—
84CA ₂	CA+MgO+MA	CA+MA+L	MA+L	MA+L
98CA ₂	CA+CA ₂ +MA	—	CA ₂ +MA+L	CA ₂ +L

[†]Sometimes it was necessary to regrind the samples to ascertain the attainment of equilibrium. This intermediate regrind is indicated by a “+” symbol. As in the previous case, the equilibrium statuses were evaluated by reflected-light microscopy and FE-SEM. Phases were identified by XRD and semi-quantitative EDS microprobe analyzer. FE-SEM, field emission scanning electron microscope; XRD, X-ray diffraction; EDS, X-ray energy-dispersive spectrometry; CA, CaAl_2O_4 ; CA₂, CaAl_4O_7 ; MA, MgAl_2O_4 ; L, liquid phase at the indicated temperature.

Fig. 9. Al_2O_3 - MgO - CaO ternary system as reported by De Aza *et al.*,^{21,22} showing the isoplethal sections CaAl_2O_4 - MgO and CaAl_4O_7 - MgO that have been experimentally established in the present work. Points M, N, W, and X that intersect the monovariant boundary lines that delimit the primary field of crystallization of MgAl_2O_4 are shown. The mentioned P3 and P4 invariant points can also be seen.

(4) The thermodynamic assessments reported in the scientific bibliography of the Al_2O_3 - MgO - CaO ternary system should be regarded as provisional and reassessment should be considered, especially on solid-phase relationships.

(5) The optimization of the scientific knowledge about the ternary system Al_2O_3 - MgO - CaO must shed light on understanding the behavior of alumina-spinel, magnesia-alumina, and magnesia-alumina-spinel castable compositions and it is also essential for manufacturing the materials reproducibly, effectively, and economically.

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