



Article Changes in the Phase Composition of Calcium Aluminoferrites Based on the Synthesis Condition and Al₂O₃/Fe₂O₃ Molar Ratio

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Abstract: The presented work concerns the study of the changes in the phase composition of calcium aluminoferrites which depend on the synthesis conditions and the selection of the Al₂O₃/Fe₂O₃ molar ratio (A/F). The A/F molar ratio extends beyond the limiting composition of C_6A_2F (6CaO·2Al₂O₃·Fe₂O) towards phases richer in Al₂O₃. An increase in the A/F ratio above unity favours the formation of other crystalline phases such as $C_{12}A_7$ and C_3A , in addition to calcium aluminoferrite. Slow cooling of melts characterised by an A/F ratio below 0.58, results in the formation of a single calcium aluminoferrite phase. Above this ratio, the presence of varying contents of $C_{12}A_7$ and C_3A phases was found. The process of rapid cooling of the melts with an A/F molar ratio approaching the value of four favours the formation of a single phase with variable chemical composition. Generally, an increase in the A/F ratio above the value of four generates the formation of a calcium aluminoferrite amorphous phase. The rapidly cooled samples with compositions of $C_{22.19}A_{10.94}F$ and $C_{14.61}A_{6.29}F$ were fully amorphous. Additionally, this study shows that as the A/F molar ratio of the melts decreases, the elemental cell volume of the calcium aluminoferrites decreases.

Keywords: calcium aluminoferrites; synthesis condition; solid solutions; X-ray diffraction

1. Introduction

In the C-A-F (CaO-Al₂O₃-Fe₂O₃) ternary system (Figure 1), a series of solid solutions are present on the line starting at the point of C₂F composition (2CaO·Fe₂O₃), and along the line joining the hypothetical C₂A (2CaO·Al₂O₃) up to a composition expressed by an A/F(Al₂O₃/Fe₂O₃) ratio of 0.69 [1]. Previous experiments showed that the line between the hypothetical C₂A and C₂F phases can be divided into three ranges [2]. The first is the range of occurrence of solid solutions of calcium aluminoferrites in the area between C₂F and C₄AF. The second range is the area of occurrence of solid solutions between C₄AF and the compound defined as C₆A₂F. Within the above area, it is also possible to delineate a compositional range between the compound C₆AF₂ and C₆A₂F.



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Figure 1. Phase diagram of the CaO-2CaO·Fe₂O₃-CaO·Al₂O₃ system [2].

This phenomenon is associated with the occurrence of calcium aluminoferrites in Portland clinker, and it is also the subject of numerous research works [3]. The third, least understood, compositional range is that of the phases occurring on the line between C_6A_2F and the hypothetical C_2A .

Studies [4,5] show that solid solutions located between C_2F and the hypothetical C_2A are beyond the limiting range of C_4AF . This can have a significant impact on the properties of Portland clinker and its hydration activity. According to Bojkova [6], calcium aluminoferrites in industrial Portland clinker should be identified with the C_6A_2F phase rather than with C_4AF , which may be explained by the use of imprecise calculation techniques for clinker phase composition determination methods.

The region in the C-A-F configuration between the hypothetical C_2A and the C_4AF phase was previously investigated by Swayz [7], Newkirk [8], and Smith [9]. The results of the aforementioned work confirmed that C_4AF is not an extreme member of a range of calcium aluminoferrite solid solutions, while the C_6A_2F phase was considered a limiting compound that is still a solid solution [10].

The C₄AF phase, which was most extensively reported in the literature, occurs as one of the elements of a series of Ca₂Fe_{2-x}Al_xO₅ solid solutions in which x takes on values ranging from 0.66 to 1.38. The crystal structure of this compound was classified into the spatial 'Icmm' group. The structure of the C₄AF phase is similar to that of C₂F and consists of perovskite-like layers. The average distance between atoms in C₄AF polyhedra, consisting of tetrahedra and octahedra, is slightly smaller than in the C₂F phase. The polyhedra forming the C₄AF structure become distorted as a result of the failure to maintain the correct proportions in the arrangement of the polyhedral elements [10].

The calcium ion is located in a deformed polyhedra containing seven oxygen ions. The average distance between the calcium and oxygen ions is assumed to be 2.461 Å. Consequently, the polyhedra in C₂F and C₄AF should be characterised by high chemical bond anisotropy, which, in combination with the electric field gradient of the Fe³⁺ ion, favours the generation of stresses within the crystal structure [11]. This results in an increase in the activity level of these compounds and the dynamics of solid-phase reactions including hydration processes. In the structure of calcium aluminoferrites, aluminium ions substitute iron ions predominantly in the tetrahedral positions up to x = 0.33, i.e., in the anionic lattice, followed by substitutions taking place evenly in both co-ordinations and involving both tetrahedral and octahedral positions.

A smaller ionic radius of Al^{3+} (0.57 Å) compared to the Fe³⁺ ion (0.67 Å) favours the accelerated migration of Al^{3+} ions from the tetrahedral to the octahedral position [12].

Figure 2 shows the results of study [2], describing the changes in the A/F ratio as a result of the substitution of Fe^{3+} ions with Al^{3+} ions in the tetrahedral and octahedral positions of calcium aluminoferrites.



Figure 2. Relationship between the value of the Al substitution factor for Fe in the tetrahedral and octahedral positions of calcium aluminoferrites according to [2].

The clinkerisation process involves the phenomenon of heterovalent isomorphic substitutions in the elemental cell of calcium aluminoferrites, which de facto disrupt the electrostatic balance and micro-symmetry of the structure. The accumulation of structural defects may favour the formation of calcium aluminoferrites in amorphous form.

Studies on the determination of elemental cell parameters of a series of C_2F solid solutions and a hypothetical ' C_2A ' in the C-A-F system were carried out by Newkirk [8], Thwaite [8], and Smith [9]. The results of these studies, together with supplemented data from the ICCD PDF-2 database, are summarized in Table 1.

Dhaca]	Parameters of the Ele	Flomontary Coll Volumo $[^{3}] \pm 0.1$		
Phase	a	b	с	$\alpha; \beta; \gamma = 90$	Elementary Cell volume [A ²] ± 0.1
C ₆ A _{2.07} F _{0.93}	5.513	14.484	5.309	90	423.9
C A E	5.480	14.350	5.220	-	_
$C_6A_2\Gamma$	5.526	14.469	5.314	90	424.8
$C_6A_{1.75}F_{1.25}$	5.548	14.490	5.331	90	428.5
	5.510	14.420	5.260	-	-
	5.580	14.500	5.340	90	432.1
$C_6A_{1.5}F_{1.5}$	5.584	14.600	5.374	-	438.1
	5.567	14.521	5.349	90	432.4
	5.565	14.514	5.346	90	431.8
$C_6A_{1.25}F_{1.75}$	5.579	14.550 ± 0.002	5.361	90	435.1
$C_6A_{1.09}F_{1.91}$	5.583	14.580	5.374	90	437.4
CAE	5.580	14.600	5.370	90	437.5
$C_6A\Gamma_2$	5.588	14.587 ± 0.002	5.375	90	438.1
$C_6A_{0.9}F_{2.1}$	5.588	14.610	5.38	90	439.2
$C_6A_{0.5}F_{2.5}$	5.595	14.679	5.403	90	443.7
	5.580	14.630	5.320	-	446.7
C = (C = C)	5.640	14.680	5.390	-	-
$C_{6}\Gamma_{3}(C_{2}\Gamma)$	5.599	14.771	5.429	-	449.0
	5.600	14.767	5.428	90	448.8

Table 1. Elementary cell parameters of a sequence of solid solutions of the $C_x A_y F_z$ type [2].

Calcium aluminoferrite phases are one of the main compounds included in several types of bonding materials, e.g., Portland cement and aluminous cement [13,14].

The problem of the varying properties of calcium aluminoferrites formed by sintering in the presence of a small amount of liquid phase and crystallising from the melt, as well as the influence of the melt cooling conditions on the type and properties of these phases, has been the subject of very few works. One of the first researchers to determine the composition of the aluminoferrite phase described by the C₄AF formula was Brownmiller [3]. The found mass ratio of Al_2O_3/Fe_2O_3 in the examined phase was 0.64, and several solid solutions between the C₂F and C₄AF compositions were also indicated. The CaO-Al₂O₃- Fe_2O_3 system was also studied by Yamauchi [11] and Swayz [7]. These authors showed that the solid solutions between C_2F and the hypothetical C_2A are beyond the 'extreme' range of C₄AF, which has a significant impact on the properties of the Portland clinker and, subsequently, on the properties of the resulting cements. Comparatively, Newkirk and Thwaite [8], noted that C_4AF is not an 'extreme' solid solution of a range of calcium aluminoferrites. According to these authors, the limiting solid solution enriched in aluminium is C_6A_2F . Considering these facts, further research directed at determining the maximum content of aluminium ions in solid solutions that correspond to the extreme composition of C_6A_2F is justified.

The present study aims to determine both the influence of the A/F molar ratio beyond the limiting composition of C_6A_2F towards Al_2O_3 -richer phases and the effect of the synthesis conditions on the phase composition of calcium aluminoferrites.

In this paper, we present the synthesis of aluminoferrites sequentially by showing the varying starting compositions of the mixtures, the melting and cooling conditions (slow or rapid cooling), and the final result in the analysis of the phases formed depending on the A/F ratio and the cooling method.

In studies planned for the near future, pro-ecological solutions for the use of chemically and structurally modified calcium aluminoferrites in the production of modern binding materials will be proposed.

2. Materials and Methods

2.1. Component Materials for Synthesis

Calcium carbonate, aluminium oxide, and iron (III) oxide with a purity of p.a. (POCh S.A. Gliwice, Poland) were used to obtain calcium aluminoferrites. The composition of the raw material mixtures was chosen to correspond to the nominal compositions for the following chemical combinations: C_2F , $C_{22}AF_{10}$, $C_{12}AF_5$, C_8AF_3 , C_6AF_2 , C_4AF , C_6A_2F , $C_{10}A_4F$, and $C_{22}A_{10}F$. The choice of the individual oxides and the molar and mass ratio A/F of the calcium aluminoferrites are given in Table 2.

Table 2. Nominal composition of calcium aluminoferrites.

Item	Nominal	Oxide Composition [% Weight]			Mass Ratio	Molar Ratio	Molar Ratio $C_{2}O/(A_{1}-O_{2} + E_{2}-O_{2})$	
	Composition –	CaO	Al ₂ O ₃	Fe ₂ O ₃	- A1203/10203	Al ₂ O ₃ /1e ₂ O ₃		
1.	C ₂ F	41.25	-	58.75	-	-	2.0	
2.	C22AF10	42.07	3.48	54.45	0.06	0.10	2.0	
3.	$C_{12}AF_5$	42.77	6.48	50.75	0.13	0.20	2.0	
4.	C_8AF_3	43.57	9.90	46.53	0.21	0.33	2.0	
5.	C_6AF_2	44.40	13.45	42.15	0.32	0.50	2.0	
6.	C_4AF	46.16	20.98	32.86	0,64	1.00	2.0	
7.	C_6A_2F	48.06	29.13	22.81	1.28	2.00	2.0	
8.	$C_8 A_3 F$	49.07	33.46	17.47	1.92	3.00	2.0	
9.	$C_{10}A_4F$	49.70	36.15	14.15	2.55	4.00	2.0	
10.	$C_{14}A_6F$	50.44	39.30	10.26	3.83	6.00	2.0	
11.	$C_{22}A_{10}F$	51.13	42.25	6.62	6.38	10.00	2.0	

The A/F molar ratio of the starting compositions of the mixtures varied in the range of 0.1 to 10.0, while the CaO/(Al₂O₃ + Fe₂O₃) constant molar ratio of two was kept.

2.2. Methods of Synthesis

Calcium aluminoferrites were obtained by melting the raw material stock. The formation of the structure and microstructure of the samples was carried out in two ways: the first involved slow cooling, while the second involved rapid cooling of the produced melts, according to the scheme shown in Figure 3.



Figure 3. Scheme for the preparation of calcium aluminoferrites.

The process of high-temperature thermal treatment of samples with a diameter of 50 mm and a height of 80 mm placed in platinum evaporators was carried out in a superkanthal furnace. The samples were prepared from a set of mixtures moistened with water at 7–8%, which were densified and then dried at 110 $^{\circ}$ C. The melting process was carried out by heating the samples at a temperature 20 °C higher than the characteristic temperature taken from the literature data [8]. The resulting melts were held at peak temperature for 2 h. The tests involved the preparation of two series of samples: slowly and rapidly cooled. Rapid cooling involved immediately removing the evaporators with the samples from the furnace and placing them in a water bath at 10 °C. Slow cooling comprised leaving the melted material in the furnace cooled at an average rate of about 2 °C/min to 1000 °C and then at a rate of about 10 °C/min to 400 °C. Once this temperature was reached, the samples were removed from the oven and cooled at room temperature. In the next step, the samples were initially crushed in an agate mortar (Conbest, Cracow, Poland) and then ground in a vibratory mill to a grain size corresponding to a 0.01 mm sieve mesh (Frisch GmbH & Co KG, Munich, Germany). Identical grinding conditions were applied for all the preparations tested.

The content of CaO, Fe_2O_3 , and Al_2O_3 in the obtained samples was determined in accordance with PN-EN 196-2:2006 [15]. The results of the actual molar ratios of the oxides in the individual variants are summarised in Table 3.

Item	Nominal	(Oxide Compositio [% Weight]	Actual Composition	
	Composition	CaO	Al ₂ O ₃	Fe ₂ O ₃	
1.	C ₂ F	40.95	-	58.55	C _{1.99} F
2.	$C_{22}AF_{10}$	41.97	3.63	54.40	C _{21.02} AF _{9.56}
3.	$C_{12}AF_5$	42.35	6.12	51.53	C _{12.58} AF _{5.37}
4.	C ₈ AF ₃	43.95	10.51	45.54	C _{7.61} AF _{2.76}
5.	C_6AF_2	44.65	15.00	40.35	C _{5.41} AF _{1.72}
6.	C_4AF	46.45	21.15	32.40	C _{4.08} A _{1.02} F
7.	C_6A_2F	47.90	30.60	21.50	C _{6.34} A _{2.23} F
8.	C ₈ A ₃ F	50.00	32.90	17.10	C _{8.33} A _{3.01} F
9.	$C_{10}A_4F$	49.69	36.40	13.91	C _{10.17} A _{4.09} F
10.	$C_{14}A_6F$	50.55	39.60	9.85	C _{14.61} A _{6.29} F
11.	$C_{22}A_{10}F$	50.50	43.30	6.20	C _{22.19} A _{10.94} F

Table 3. Chemical composition of the synthesized calcium aluminoferrites.

It can be seen that the actual molar compositions of the calcium aluminoferrites obtained are in approximate agreement with the nominal compositions, justifying a study of their phase composition.

2.3. Methods of Determination of the Sintering, Melting, and Flow Temperatures of the Samples

The homogenised samples were examined in a high-temperature heating microscope (Hesse Instrumente, Osterode am Harz, Germany). The samples used for this study were 1 g cube-shaped samples, which were obtained by powder moulding in a punch press (Metimex, Pyskowice, Poland). The thermal processing of the samples was carried out by a linear temperature increase at a rate of $5 \,^{\circ}$ C/min. The heating microscope was equipped with specialised software allowing quantitative measurements of the outline of the surface area (in %) and the changes in the shape of the top line of the moulded sample cube. This enabled the temperatures of the onset of sintering, melting, and flowing of the samples to be determined with high precision.

Computer analysis of the heat treatment process allows curves to be plotted with "x" and "y" coordinates, representing, respectively, the current temperature of the sample and changes in the outline of the pellet's surface area. The computer software allowed for directly obtaining information on the amount of the separated liquid phase of the examined sample based on changes in the outline of the analysed surface area. It was assumed that at the sample's melting temperature, the sample would melt completely, which corresponds to a 100% liquid phase separation.

It can be seen from the diagram shown in Figure 4, that there is no linear progression (red line) in the process from the start of sintering of the calcium aluminoferrite sample to its complete melting.



Temperature [°C]

Figure 4. An example of the determination of the characteristic heat treatment temperature C_6AF_2 , where T_s —temperature of the start of sintering (experimental); T_{sp} —temperature of the start of sintering (calculated); T_t —temperature of melting; T_p —temperature of flow. 1—sample shape index; 2—sample height; 3—lateral lesions of the sample.

The procedure for determination of the heat treatment temperature of variants containing a limited amount of liquid phase was as described below. As a first step, it was assumed that the process from the start of sintering to the complete melting of the sample could be represented as a line segment of length corresponding to 100% (*y*-axis). In the next step, it was determined that the heat treatment temperature corresponds to half the length of the line segment (50%) and then, by considering the profile of the curves, its position can be determined and then the desired temperature can be determined.

The sintering, melting, and flow temperatures of the tested samples, determined as previously described, are summarised in Table 4 and Figure 5.

Phases with	a Composition		Characteristic Temperatures [°C]							
Nominal	Actual	Start of Sintering (Experimental)	Start of Sintering (Calculated)	Melting	Flow					
C ₂ F	C _{1.99} F	990	1380	1418	1430					
$C_{22}AF_{10}$	C _{21.02} AF _{9.56}	990	1376	1405	1422					
$C_{12}AF_5$	C _{12.58} AF _{5.37}	990	1375	1405	1421					
C_8AF_3	C _{7.61} AF _{2.76}	997	1373	1400	1415					
C_6AF_2	C _{5.41} AF _{1.72}	990	1375	1383	1412					
$C_4 AF$	$C_{4.08}A_{1.02}F$	988	1376	1392	1405					
C_6A_2F	C _{6.34} A _{2.23} F	1005	1375	1385	1402					
C_8A_3F	C _{8.33} A _{3.01} F	990	1372	1382	1396					
$C_{10}A_4F$	C _{10.17} A _{4.09} F	955	1375	1379	1383					
$C_{14}A_6F$	C _{14.61} A _{6.29} F	940	1375	1377	1382					
$C_{22}A_{10}F$	C _{22,19} A _{10,94} F	951	1380	1386	1393					
"C ₂ A"	$C_{1.96}A_{1.04}$	1072	1420	1431	1434					

Table 4. The sintering, melting, and flow temperatures of the examined calcium aluminoferrites.

Note: The error of the method used is $[\pm 2.5 \circ C]$.



Figure 5. Dependence of characteristic temperatures of thermal processes on the chemical composition of the formulations.

The results of the determination of the melting temperatures of the samples obtained in this study, after considering measurement errors, are in rough agreement with the literature data reported by Newkirk and Thwait [8], who determined melting temperatures for several phases (C_2F —1438 °C, C_4AF —1403 °C, and C_2A about 1440 °C).

The data in Table 4 and Figure 5 indicate that there is a temperature interval of about 10 °C between the melting point and the flow temperature of samples covering the composition range from C_2F to C_8AF_3 . For samples with compositions ranging from C_2A to $C_{10}A_4$, this interval is reduced. In addition, a temperature interval, around 15 °C, is observed between the temperature of the thermal treatment with a limited liquid phase and the melting temperature for the samples in the composition range from C_2A to $C_{10}A_4F$. In contrast, for several samples from C_8AF_3 to C_2F , this interval gradually increases to 50 °C. It can be seen that the gradual increase in the above interval is associated with an increase in Fe₂O₃ content in a series of successive thermally treated phases.

2.4. Method for XRD Phase Composition Studies

X-ray measurements were performed on samples with grain sizes below 0.020 mm. A vibratory agate mill (Frisch, Germany) was used to grind 3 g of samples and an additional

15% (by weight) of metallic Si ('Silicon Powder' SRM 640, X-ray Diffraction Standard, NIST, Gaithersburg, MD, USA). A grinding time of 1.5 h was applied. A vibrating mill with an external diameter of 95 mm and a grinding ball diameter of 50 mm was used; the weight of the grinding ball was 171 g. The vibration mill was characterised by an amplitude of 0.2 mm at a vibration frequency of 2000 Hz.

All samples without and with added standards were prepared in an analogous manner. Ground samples of approximately 1 g were placed in a flat measuring holder and immediately subjected to measurements to avoid prolonged contact with humidity.

XRD tests were carried out on a "PHILIPS" apparatus (Amsterdam, The Netherlands), consisting of a PW 1140/00/60 X-ray tube power supply and an upgraded PW 1050/50 vertical goniometer. The goniometer was equipped with software for fully automatic control with simultaneous digital recording of measurement data. The equipment setup included a vertically mounted 'PHILIPS' X-ray tube with cobalt anticathode (Co) and a wavelength of $K_{\alpha} = 1.7910$ Å. An 'Fe' filter preventing the fluorescence effect from appearing in preparations containing large amounts of iron was used.

A PW 2216/20 'fine focus' X-ray tube with a power of 1200 W and a window size of 0.4×8.0 mm and a focusing area of 3.2 mm^2 was used, which, at an incidence angle of 6°, allowed the generation of a radiation beam with a width of 0.05 mm. The 1000 W lamp was operated at 40 kV with a cathode current of 25 mA. Measurements were carried out for a fixed angular range, from 10° to 80°20. For quantitative studies, a 20% addition of powdered metallic silicon was used with analogous powder preparation conditions.

Based on the X-ray data, a qualitative analysis of the samples was carried out to detect the presence of the relevant phases and a quantitative analysis to determine the mass proportion of crystalline and 'amorphous' phases, as well as the lattice parameters of the elementary cells of the detected phases. The Rietveld method [16–18] was used for quantitative data analysis. Specialised software such as X'PertHighScore Plus v. 2.1 from 'Philips' [19], and EXPGUI v. 3.0 from Los Alamos National Laboratory were used to process the data. In addition, the software "Jana 2006" from the Institute of Physics ASCR in Prague [20] and ANALYSIS-RayfleX v. 2.8 [21], as well as "MERCURY 3.7" Crystal Structure Visualisation (CCDC) [22,23] were also used.

3. Results

Figures 6 and 7 summarize the X-ray diffractograms of the samples, which were subjected to slow or rapid cooling, respectively.



Figure 6. X-ray diffraction patterns registered for calcium aluminoferrites cooled at a slow rate.



Figure 7. X-ray diffraction patterns of calcium aluminoferrites cooled at a rapid rate.

The results of the quantification of the phases formed are given in Tables 5 and 6.

Table 5. Composition of C _x A _y	F _z for calcium alumino	ferrites cooled at a slow rate
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Item A	Actual Composition	Molar Ratio	Pha	se Composi [% Weight]	ition	Molar Phas	Y/Z		
		AI_2O_3/Fe_2O_3	$C_{12}A_7$	C ₃ A	$C_x A_y F_z$	x	Y	Z	
1.	C _{1.99} F	-	-	-	-	1.991	-	-	-
2.	C _{21.02} AF _{9.56}	0.10	-	-	100.0	21.021	1.000	9.568	0.10
3.	C _{12.58} AF _{5.37}	0.19	-	-	100.0	12.582	1.000	5.375	0.19
4.	C _{7,61} AF _{2.766}	0.36	-	-	100.0	7.603	1.000	2.766	0.36
5.	C _{5.41} AF _{1.72}	0.58	-	-	100.0	5.412	1.000	1.717	0.58
6.	C _{4.08} A _{1.02} F	1.02	0.5	-	99.5	4.030	1.009	1.0	1.00
7.	C _{6.34} A _{2.23} F	2.23	15.0	-	85.0	5.353	1.666	1.0	1.67
8.	C _{8.33} A _{3.01} F	3.01	21.1	13.2	65.7	5.218	1.562	1.0	1.56
9.	C _{10.17} A _{4.09} F	4.09	32.8	12.0	55.2	5.283	1.687	1.0	1.69
10.	C _{14.61} A _{6.29} F	6.29	50.5	8.8	40.7	5.828	1.636	1.0	1.64
11.	$C_{22.19}A_{10.94}F$	10.94	65.6	8.0	26.4	6.191	1.646	1.0	1.65

Table 6. Composition of $C_x A_y F_z$ for calcium aluminoferrites cooled at a rapid rate.

Item	Actual	Molar Ratio	Phase Composition [% Weight]				Molar I	Y/Z		
	Composition	$A1_2O_3/Fe_2O_3$	C ₁₂ A ₇	C ₃ A	$C_x A_y F_z$	Amorphous	х	Y	Z	
1.	C _{1.99} F	-	-	-	-	-	1.991	-	-	-
2.	C21.02AF9.56	0.10	-	-	100.0	-	21.021	1.000	9.568	0.10
3.	C12.58AF5.37	0.19	-	-	100.0	-	12.582	1.000	5.375	0.19
4.	C _{7.61} AF _{2.766}	0.36	-	-	100.0	-	7.603	1.000	2.766	0.36
5.	C _{5.41} AF _{1.72}	0.58	-	-	100.0	-	5.412	1.000	1.717	0.58
6.	C _{4.08} A _{1.02} F	1.02	-	-	100.0	-	4.030	1.009	1.000	1.00
7.	C _{6.34} A _{2.23} F	2.23	-	-	100.0	-	6.337	2.226	1.000	2.23
8.	C _{8.33} A _{3.01} F	3.01	-	-	100.0	-	8.329	3.010	1.000	3.01
9.	C _{10.17} A _{4.09} F	4.09	8.9	-	50.1	41	-	-	-	4.09
10.	C14.61A6.29F	6.29	-	-	-	100	-	-	-	6.29
11.	$C_{22.19}A_{10.94}F$	10.94	-	-	-	100	-	-	-	10.90

In samples numbered seven to eleven, the composition of the aluminoferrite phase is altered compared to the nominal composition and, in addition, for the $C_xA_yF_z$ phase, the A/F ratio is approximately 1.64.

As the A/F molar ratio increases above one, an increase in the amount of mayenite is observed, with a simultaneous decrease in the concentration of calcium aluminoferrites.

The C₃A phase is separated only when the A/F molar ratio is above three. A further increase in the A/F ratio induces a decrease in the mass proportion of the C₃A phase. For the samples subjected to rapid cooling, only the calcium aluminoferrite phase was found, with the exception of sample number nine with a composition of C_{10.17}A_{4.09}F, in which an amorphous phase was identified in addition to the crystalline calcium aluminoferrite phase and C₁₂A₇. In the last two samples, where the A/F molar ratio is six and ten, only amorphous calcium aluminoferrite is present.

Tables 7 and 8 summarise the determined interplane distances d and the corresponding intensities as a function of the A/F molar ratio.

1 2 3 4	5	6
Phase $h k l$ $C_{1.99}F$ $C_{21.02}AF_{9.56}$ $C_{12.58}AF_{5.37}$ $C_{7.61}AF_{2.76}$	C _{5.41} AF _{1.72}	$C_{4.03}A_{1.01}F$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	6] d/[Å] [%]	d I [Å] [%]
ferrite 0 2 0 7.431 15 7.409 28 7.377 21 7.338 38	3 7.299 48	7.265 64
C ₁₂ A ₇ 211		4.899 10
ferrite		
ferrite 1 3 0 3.708 18 3.694 33 3.683 22 3.673 22	2 3.659 28	3.646 20
ferrite		
ferrite		
ferrite 200 2.808 37 2.805 47 2.800 52 2.798 28	3 2.792 47	2.783 36
C ₃ A 440		
ferrite 0 0 2 2.709 80 2.701 50 2.694 59 2.691 32	2 2.685 50	2.677 39
territe 1 4 1 2.680 100 2.676 100 2.670 100 2.661 10	0 2.651 100	2.644 100
territe 150 2.613 14 2.606 20 2.601 26 2.592 20	2.578 38	2.573 20
ferrite 211 2.451 15 2.449 15 2.446 10 2.444 10) 2.441 15	2.439 10
ferrite 2 4 0 2.234 10 2.228 10 2.224 12 2.217 15	5 2.214 10 2.1(4 10	2.209 12
ferrite 0.4.2 2.188 10 2.186 18 2.180 10 2.169 12	2 2.164 18	2.155 11
ferrite $1.6.1$ 2.082 1.6 2.076 2.071 27 2.062 2.071	3 2.054 36	2.048 37
ferrite		
ferrite 2.2.2 1.908 10 1.901 13 1.897 10 1.889 10) 1.873 13	1.865 10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$) 1.735 15	1.732 11
7 8 9 10	11	
Phase h k l C _{5.35} A _{1.66} F C _{5.22} A _{1.56} F C _{5.28} A _{1.68} F C _{5.83} A _{1.64} F	C _{6.19} A _{1.65} F	
d I d I d I d I [Å] [%] [Å] [%] [Å] [%] [Å] [%	d I 5] [Å] [%]	
ferrite 0 2 0 7 248 38 7 224 62 7 199 47 7 192 55	7 7 194 32	
$C_{12}A_7$ 211 4.903 17 4.906 35 4.884 45 4.878 10	0 4.894 100	
ferrite 3.779 15	5 3.794 13	
ferrite 1 3 0 3.639 22 3.632 20 3.620 22 3.613 21	3.615 12	
ferrite 3.199 20) 3.202 20	
ferrite 2.994 31	2.995 39	
ferrite 200 2.770 34 2.762 38 2.759 58 2.757 32	2 2.758 19	
C ₃ A 440 2.698 27 2.683 30 2.674 32	2 2.762 27	
ferrite 0 0 2 2.659 36 2.653 42 2.651 40 2.649 79	2.652 76	
ferrite 1 4 1 2.633 78 2.628 100 2.621 84 2.618 84	2.616 49	
ferrite 1 5 0 2.565 30 2.561 22 2.554 22 2.553 27	2.556 23	
ferrite 211 2.435 10 2.429 15 2.420 20 2.419 35	2.421 38	
ferrite 2 4 0 2.198 15 2.194 17 2.186 30 2.186 45	5 2.189 35	
ferrite 0 4 2 2.146 12 2.142 14 2.137 18 2.135 20) 2.138 11	
ferrite 161 2.042 21 2.039 60 2.033 31 2.031 50		
) 2.033 19	
territe 1.904 42	2.033 19 2.1.909 35	
territe - - - - 1.904 42 ferrite 2 2 2 1.853 10 1.851 13 1.847 13 1.849 14	2.033 19 2 1.909 35 4 - -	

Table 7. Values of *d* and intensity *I* * for calcium aluminoferrites cooled at a slow rate.

* Note: In accordance with the ICDD Commission guidelines, only reflections with an intensity of more than 10% are included.

		1		2	2	3	6	4	ł	5	5	6	
Phase	h k l	C _{1.9}	99F	C21.02AF9.56		C _{12.58}	AF _{5.37}	C _{7.61}	AF _{2.76}	C _{5.41} A	AF _{1.72}	$C_{4.08}A_{1.02}F$	
1 Hube	<i>n</i> K i	d	Ι	đ	Ι	d	Ι	d	Ι	d	Ι	d	Ι
		[Å]	[%]	[Å]	[%]	[Å]	[%]	[Å]	[%]	[Å]	[%]	[Å]	[%]
ferrite	020	7.431	15	7.409	30	7.369	64	7.349	47	7.289	52	7.255	50
$C_{12}A_{7}$	211	-	-	-	-	-	-	-	-	-	-	-	-
ferrite	-	-	-	-	-	-	-	-	-	-	-	-	-
ferrite	130	3.695	47	3.693	26	3.686	21	3.678	22	3.662	24	3.652	17
ferrite	-	-	-	-	-	-	-	-	-	-	-	-	-
ferrite	-	-	-	-	-	-	-	-	-	-	-	-	-
ferrite	200	2.804	48	2.803	51	2.805	29	2.801	44	2.793	33	2.778	36
ferrite	002	2.716	60	2.715	34	2.703	44	2.694	47	2.681	30	2.674	37
ferrite	141	2.679	100	2.676	100	2.669	100	2.664	100	2.656	100	2.642	100
ferrite	150	2.614	13	2.611	28	2.601	14	2.595	20	2.584	12	2.574	14
ferrite	211	2.450	10	2.448	15	2.445	10	2.443	15	2.439	10	2.436	10
ferrite	240	2.229	10	2.214	10	2.209	12	2.194	17	2.219	10	2.208	11
ferrite	042	2.187	13	2.184	13	2.155	11	2.136	15	2.167	12	2.163	11
ferrite	161	2.080	21	2.075	40	2.071	21	2.065	24	2.059	23	2.048	22
ferrite	-	-	-	-	-	-	-	-	-	-	-	-	-
ferrite	222	1.906	24	1.899	83	1.895	18	1.890	21	1.874	10	1.862	10
ferrite	330	1.745	10	1.745	15	1.744	11	1.743	10	1.739	10	1.732	11
		7	7	8	3	9)	1	0	1	1		
Phase	h k l	C _{6.34}	A _{2.23} F	C _{8.33}	A _{3.01} F	C _{10.17}	A _{4.09} F	C _{14.61} A	_{6.29} F **	C _{22.19} A ₁	10.94F **		
		đ	I	đ	Ι	đ	Ι	ļ	Ι	d	Ι		
		[Å]	[%]	[Å]	[%]	[Å]	[%]	[Å]	[%]	[Å]	[%]		
ferrite	020	7.242	67	7.240	62	7.237	34	-	-	-	-		
$C_{12}A_{7}$	211	-	-	-	-	4.883	20	-	-	-	-		
ferrite	-	-	-	-	-	-	-	-	-	-	-		
ferrite	130	3.637	25	3.634	20	3.636	22	-	-	-	-		
ferrite	-	-	-	-	-	-	-	-	-	-	-		
ferrite	-	-	-	-	-	-	-	-	-	-	-		
ferrite	200	2.766	44	2.760	38	2.758	47	-	-	-	-		
ferrite	002	2.659	38	2.654	42	2.655	24	-	-	-	-		
ferrite	141	2.633	100	2.628	100	2.629	100	-	-	-	-		
ferrite	150	2.566	25	2.562	22	2.563	18	-	-	-	-		
ferrite	211	2.420	10	2.419	15	2.420	12	-	-	-	-		
ferrite	240	2.200	17	2.195	17	2.196	24	-	-	-	-		
ferrite	042	2.145	13	2.142	14	2.143	20	-	-	-	-		
ferrite	161	2.043	28	2.041	60	2.044	26	-	-	-	-		
ferrite	-	-	-	-	-	-	-	-	-	-	-		
ferrite	222	1.855	10	1.851	13	1.852	13	-	-	-	-		
ferrite	330	1.725	10	1.723	13	1.724	10	-	-	-	-		

Table 8. Values of *d* and intensity *I* * for calcium aluminoferrites cooled at a rapid rate.

* In accordance with the ICDD Commission guidelines, reflections with an intensity of more than 10% are included. ** Samples with compositions of C_{22.19}A_{10.94}F and C_{14.61}A_{6.29}F were characterised by the presence of an amorphous phase as a result of rapid cooling.

From these data, it can be seen that as the Al_2O_3 content of the calcium aluminoferrite phases increases, there is a decrease in the *d* values. For example, for the plane (141), to which the highest intensity corresponds, the *d* values vary from 2.680 Å to 2.618 Å.

Figures 8 and 9 illustrate the variation of *d* for reflex (141) as a function of the Al_2O_3/Fe_2O_3 molar ratio for calcium aluminoferrite subjected to slow or rapid cooling.



Figure 8. Changes in elemental cell dimensions of calcium aluminoferrites as a function of the A/F molar ratio after slow and rapid cooling.



Figure 9. Changes in *d* values for reflex (141) vs. A/F ratio for calcium aluminoferrites cooled at a slow rate.

These relations show an approximately linear course and can, therefore, be described by Vegard's rule [23,24]. The fit of the experimental data for slowly cooled samples is better compared to rapidly cooled samples. This can be explained by the slow formation of the crystal structure of these samples. For samples subjected to rapid cooling, the weaker fit of the linear relationship is due to the need for immediate crystallisation of the phases from the melt and the proportion of the amorphous phase in the test samples. Deviations from the Vegard rule relate, among other things, to the case of systems that do not exhibit isomorphism. The appearance of additional crystalline phases in the calcium aluminoferrite solid solutions studied results in a deviation from the Vegard rule [24,25]. The noticeable changes in the interplanar distances 'd' of the calcium aluminoferrites phase are due to changes in their elemental cell parameters, most likely as a result of differences in the ionic radiuses of the aluminium and iron (III) cations [24,25].

The results of the determinations of the elemental cell parameters of the calcium aluminoferrite phases subjected to slow and rapid cooling are included in Table 9.

Samula No	DI		Cell Paramete	rs in [Å] ±0.0	040	Vroent.	Proent	Crystallographic	
Sample No.	Phase -	a ₀ [Å]	c ₀ [Å]	b ₀ [Å]	$\alpha = \beta = \gamma [^{o}]$	[Å ³]	Proent.	System	
			Sam	ples subjected	to slow cooling				
1	C _{1.99} F	5.4765	5.5989	14.7322	90	451.7242	3.9890	orthorhombic	
3	C _{12.58} AF _{5.37}	5.4495	5.5911	14.7112	90	448.2311	3.9190	orthorhombic	
5	C _{5.41} AF _{1.72}	5.4031	5.5775	14.6776	90	442.3210	3.7670	orthorhombic	
6	$C_{4.08}A_{1.02}F$	5.3654	5.5673	14.6466	90	437.5055	3.6800	orthorhombic	
7	C _{6.34} A _{2.23} F	5.3133	5.5515	14.6016	90	430.7002	3.5990	orthorhombic	
8	C _{8.33} A _{3.01} F	5.2727	5.5223	14.5552	90	423.8100	3.5900	orthorhombic	
9	$C_{10.17}A_{4.09}F$	5.2489	5.5070	14.5279	90	419.9390	3.5660	orthorhombic	
			Samj	ples subjected	to rapid cooling				
1	C _{1.99} F	5.4424	5.6272	14.7382	90	451.3643	3.9920	orthorhombic	
3	C _{12.58} AF _{5.37}	5.4238	5.6140	14.6997	90	447.5942	3.9240	orthorhombic	
5	$C_{5.41}AF_{1.72}$	5.3936	5.5870	14.6245	90	440.6953	3.7800	orthorhombic	
6	$C_{4.08}A_{1.02}F$	5.3704	5.5679	14.5676	90	435.5981	3.6970	orthorhombic	
7	C _{6.34} A _{2.23} F	5.3420	5.5386	14.4977	90	428.9696	3.6140	orthorhombic	
8	$C_{8.33}A_{3.01}F$	5.3155	5.4965	14.4334	90	421.6955	3.6080	orthorhombic	
9	$C_{10.17}A_{4.09}F$	5.2947	5.4716	14.3918	90	416.9373	3.5910	orthorhombic	

 Table 9. Values of elemental cell lattice parameters for calcium aluminoferrites after slow and rapid cooling.

These values are in good agreement with the literature data [8,9] and follow the interpretation related to the phenomenon of shifting extremes of the calcium aluminoferrite phase peaks towards higher 2 θ angles. Analysis of the data in Table 9 indicates changes in the linear dimensions of the elemental cells along all a_0 , b_0 , and c_0 axes, which translates into changes in the volume of the V_{roent}. cells and their X-ray densities ρ_{roent} . Figures 9 and 10 illustrate the range of differences in the dimensions of the a_0 , b_0 , and c_0 axes of the elemental cells of the examined phases as a function of changes in the A/F ratio and the conditions of the cooling process of the studied samples.



Figure 10. Changes in *d* values for reflex (141) vs. A/F ratio for calcium aluminoferrites cooled at a rapid rate.

A decrease in all elementary cell dimensions is observed. The largest changes were recorded for the a_0 and c_0 axes and the smallest for the b_0 axis.

above changes is nearly linear, and the underlying reasons for the deviation should be sought in measurement errors. It can also be seen that the above dependencies are similar for the a_0 and b_0 axes, while they differ for the c_0 axis. The range of changes in the linear dimensions of the elemental cells of calcium aluminoferrites, for which the A/F ratio varies from 0.1 to 4.09, is for axes $a_0 = 0.228$ Å, $c_0 = 0.092$ Å, and $b_0 = 0.204$ Å. As shown in numerous studies [8–12], the reason for these changes is the substitution of Fe³⁺ ions by Al³⁺ ions, which have a smaller ionic diameter than that of iron (III) ions. After rapid crystallisation of the sample from the melt, the phenomenon of a shift in the extremes of all the peaks originating from the calcium aluminoferrites phases towards higher 20 angles can be observed.

The variation of the 'd' parameters for the (141) peak with I = 100% as a function of the A/F molar ratio in calcium aluminoferrites previously melted and then rapidly cooled is shown in Table 8. Again, with the appearance of amorphous phases, the nature of the 'truncated' curve illustrating this relationship indicates the presence of calcium aluminoferrite phases that belong to solid solutions. Above this A/F ratio of >4.01, amorphous phases are released.

The correlations presented above indicate that the changes in the parameters of the a_0 , b_0 , and c_0 axes of elemental aluminoferrite cells subjected to melting and then rapid cooling follow the same principle of a decrease in the linear dimensions of all three axes with an increase in the A/F ratio of the studied phases. As can be seen from Figure 9, the changes for the a_0 and c_0 axes follow an almost linear course and the course of changes in linear dimensions for the longest b_0 axis is different. The range of changes of the cells of calcium aluminoferrites, for which the A/F ratio varies from 0.1 to 4.09, is, for the a_0 and c_0 axes, approximately 0.148 Å and 0.155 Å, respectively, and for the b_0 axis = 0.346 Å.

The results obtained show that the dimensions of the aluminoferrite elementary cells undergo significant changes when the melts are rapidly cooled. If we compare these results with the decrease in the linear dimensions of the elemental cell axes of aluminoferrites slowly cooled as a result of the substitution of Al^{3+} for Fe^{3+} , the differences recorded must be considered to be very large. These differences are for the axes $a_0 = 0.1818$ Å, $c_0 = 0.1273$ Å, and $b_0 = 0.3404$ Å and are large enough to be the result of additional deformation and distortion of the elemental cells of the calcium aluminoferrite phases subjected to rapid cooling.

The results of the study allow us to conclude that in all the analysed samples, irrespective of the cooling method, the presence of unreacted oxides of CaO, α -Al₂O₃, Fe₂O₃, and metallic iron was not identified in the phase composition of the samples. The absence of these oxides in the mineral compositions of the melts should be related to the fact that the heat-treated samples fully reacted under the appropriate process conditions.

As a result of the melting of the samples, irrespective of the applied cooling method, only calcium aluminoferrites with varying chemical compositions formed for an A/F molar ratio from 0.10 to 1.02. The formation of these phases in the given A/F ratio range is not accompanied by the simultaneous release of other additional compounds. Based on an in-depth analysis of the changes in the elementary cell parameters of the phases, they were considered to belong to the $C_6A_xF_{3-x}$ group where 0 < x < 3 of the calcium aluminoferrites of the solid solution family occurring between C_2F and the hypothetical C_2A .

Slow cooling of calcium aluminoferrite melts characterised by an A/F ratio \geq 2.23 led to the separation of two or three different phases. As the A/F ratio increased from 1.02 to 10.94, a calcium aluminoferrite phase with a slightly varying chemical composition was formed in the analysed samples in addition to mayenite (C₁₂A₇) and tricalcium aluminate (C₃A).

Calculations show that its composition, treated as an 'average composition', is close to that of the phase with formula $C_{5,8}A_{1,7}F$. It appears that, in the analysed area of variation

of the A/F ratio, the content of the mayenite phase increases to a value of about 65% (wt.) and, in the extreme case, the C_3A level reaches about 12% (wt.).

Qualitative and quantitative analysis of the phase compositions of the samples subjected to rapid cooling with A/F molar ratios ranging between 0.10 and 4.09 indicates the presence of only an aluminoferrite phase of variable chemical composition, which is free of admixtures of other compounds. The previously mentioned area of A/F ratio variation covers about one-third of the total study range. In contrast to all other rapidly cooled preparations, for which the A/F ratio is equal to 4.09, mayenite and a glassy phase are released in addition to calcium aluminoferrites. Rapid cooling of the melts with a further increase in the A/F molar ratio above 4.09 contributes to a change in the physical state and a transition of the preparations to an amorphous form.

It can be concluded that by using the correct synthesis and cooling procedure, the phase composition of the resulting melts can be influenced in a controlled manner. In the case of the present work, synthesis by melting and rapid cooling of the melts led to an aluminoferrite phase that was free of admixtures of other compounds in the range of A/F molar ratios from 1.02 to 4.09.

X-ray studies confirmed the low efficiency of obtaining good quality calcium aluminoferrite preparations during a long-time synthesis, lasting 6 h, based on sintering at a temperature approximately 40 $^{\circ}$ C lower than the melting point of the samples.

Based on the observation of the phenomenon of shifting peak extremes originating from calcium aluminoferrites and the analysis of changes in elementary cell parameters due to changes in the A/F ratio, it can be concluded that the studied phases belong to the family of solid solutions of calcium aluminoferrites of the $C_6A_xF_{3-x}$ group, where 0 < x < 3.

The study linked a decrease in the linear dimensions of the elemental cells of calcium aluminoferrite solid solutions to an increase in their Al_2O_3 content. Considering the above, the formation of compounds belonging to the family of calcium aluminoferrite solid solutions described by the formula $C_6A_xF_{3-x}$, where 0 < x < 3 should be associated with the effect of substitution in the C_2F elementary cell of some Fe³⁺ ions with Al^{3+} ions of smaller ionic radius [2,8].

It also seems reasonable that with changes in the linear dimensions of the a_0 , b_0 , and c_0 axes, while maintaining the same crystallographic arrangement, there will be a change in the volume of the elemental cell and its X-ray density.

The changes in the relationship between the linear dimensions of the calcium aluminoferrite elemental cells and the A/F molar ratio of the melted preparations, which were subjected to slow and rapid cooling, as discussed above, indicate the existence of differences that increase with increasing A/F molar ratio in the aluminoferrite phases.

4. Discussion

This is the first known study concerning the changes in the phase composition of calcium aluminoferrites depending on the synthesis conditions and the selection of the Al_2O_3/Fe_2O_3 molar ratio (A/F), which extends beyond the limiting composition of C_6A_2F towards phases richer in Al_2O_3 . There is practically no, or scarce, literature data on this subject.

As a result of the application of an appropriate thermal treatment procedure and cooling of the preparations, a series of phases belonging to the calcium aluminoferrite group were obtained, described by the formula $C_6A_xF_{3-x}$, where 0 < x < 3, in which the molar ratio A/F varied from 0.10 to 10.94, while the constant molar ratio CaO/Al₂O₃ + Fe₂O₃ of 2.0 was kept.

The qualitative and quantitative roentgenographic studies that were carried out confirmed the different phase compositions of the preparations obtained, in that in some cases samples were obtained consisting of only calcium aluminoferrites, or multiphase preparations consisting of a mixture of mayenite ($C_{12}A_7$), tricalcium aluminate (C_3A), and ($C_xA_yF_z$) calcium aluminoferrite phase. In extreme cases, partially or completely amorphous preparations were obtained. It was proven that the phase composition of the samples depended primarily on the A/F molar ratio, which characterises the oxide contributions in the sample, as well as on the applied thermal treatment. Slowly cooled samples were characterised by the appearance of phases derived exclusively from calcium aluminoferrites when the molar ratio A/F was in the range of 0.10 to 0.58. A further increase in this A/F ratio range from 0.58 to 2.23 favoured the appearance of mayenite ($C_{12}A_7$) in addition to the calcium aluminoferrite phase. In the range of changes in the A/F molar ratio from 3.01 to 10.94, the co-occurrence of $C_{12}A_7$, C_3A , and the aluminoferrite phase is observed. From the X-ray quantitative analysis, it can be concluded that, with an increase in the A/F ratio from 1.02 to 10.94, there is a successive decrease in the mass proportion of the aluminoferrite phase (from 99.5% to 26.4%) with a concomitant increase in the amount of mayenite (from 0.5% to 65.6%). Furthermore, these changes are accompanied by a decrease in C_3A content from 13.2% to 8.0%.

The cell parameters of the elementary phases of calcium aluminoferrites, determined using the Rietveld method, showed that there is a gradual decrease in the linear dimensions of the cells in the region of single-phase aluminoferrite existence (A/F changes from 0.10 to 0.58) and the difference in these changes with respect to the individual axes is $a_0 = 0.228$ Å, $b_0 = 0.204$ Å, and $c_0 = 0.092$ Å. The observed changes in the linear dimensions of the elemental cells are a result of the substitution of Fe³⁺ ions with Al³⁺ ions of smaller ionic radius in calcium aluminoferrites characterised by variations in the A/F ratio.

The phase compositions of rapidly cooled samples behave differently compared to the slowly cooled samples. In the range of an A/F molar ratio from 0.10 to 3.01 (inclusive), the analysed preparations consist of 100% aluminoferrite phases. It should be noted that, in this case, the range of single-phase calcium aluminoferrite phases was extended from A/F = 2.23 to a level of A/F = 3.01. At an A/F ratio of 4.09% mayenite, 50% aluminoferrite, and 40% of an amorphous phase co-occur. With a further increase in the A/F molar ratio between 4.09 and 10.94, there is a change in the physical state of the samples due to their transformation to the amorphous form.

Relationships between changes in the linear dimensions of the elemental cell axes of calcium aluminoferrites resulting from changes in the A/F molar ratio during melting and slow or rapid cooling indicate significant differences, which increase with increasing A/F ratios in the studied phases.

Upon rapid cooling of calcium aluminoferrite samples, the linear dimensions of the elementary cell phase axes shorten for the a_0 axis by about 0.071 Å, with a concomitant lengthening of the c_0 axis by about 0.060 Å and of the b_0 axis by about 0.143 Å. The above leads to the conclusion that during rapid cooling of calcium aluminoferrite-based melts, structural deformations occur that favour an increase in the degree of defectivity of the crystalline structure of the studied phases, which may lead to an increase in their chemical reactivity in various reactions environments. When the A/F molar ratio is kept between 4.09 and 10.94, partially or completely amorphous phases are released in the preparations obtained after rapid cooling.

This study comprises the character of basic research, as it focuses on the influence of the admixing of calcium ferrate phases with aluminium ions. The analysis of the calcium aluminoferrites line as well as the extent to which their solid solutions occur on the C₂F–"C₂A" line, due to the occurrence of this type of phase in aluminous cements as well as in Portland cements from the point of view of cement chemistry and its technology, is a key issue. An appropriate modelling of the calcium aluminoferrite phases can contribute to the preparation of a stand-alone binder or activator for the setting and hardening of Portland cements.

Concerning future practical implications, the method of synthesis and appropriately selected waste materials (as additives) will lead to the production of an alternative binder with the characteristics of aluminous cements, such as fondu. In further stages, it is planned to analyse the hydration activity of the calcium aluminoferrites obtained in processes involving water.

Produced samples will be subjected to hydraulic activity tests. Tests will be performed towards calorimetric analysis of the hydrating slurries and the influence of cooling conditions and the chemical composition of the calcium aluminoferrite phases and their mixtures.

Selected samples of the most active phases will be tested in mixtures with Portland cement with low C_3A contents. Pastes from different phases of calcium aluminoferrites and their mixtures, as well as the mixtures of calcium aluminoferrites with Portland cement, will be analysed for mechanical strength and durability against chemical corrosion.

5. Conclusions

The results of this study allowed for the following conclusions:

- 1. A significant effect of the conditions under which calcium aluminoferrites were obtained on their phase composition was observed.
- 2. In slowly cooled samples with A/F ratios of 0.10 to 0.58, calcium aluminoferrite phases are released, while in other cases calcium aluminoferrites co-occur with $C_{12}A_7$ and C_3A .
- 3. Under rapid cooling conditions for samples with A/F ratios between 0.10 and 3.01, only calcium aluminoferrites are formed. In the case of the sample with a composition of $C_{10.17}A_{4.09}F$, calcium aluminoferrite co-occurs with $C_{12}A_7$ calcium aluminate and an amorphous phase. Samples with A/F ratios between 6.29 and 10.94 are amorphous.
- 4. Quantitative roentgenographic studies of calcium aluminoferrites have shown that changes in elemental cell parameters are a consequence of the cooling conditions used and changes in the A/F molar ratio. Significant structural changes are observed for samples subjected to rapid cooling.

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