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RESEARCH ON THE SYNTHESIS OF CORDIERITE IN REFRACTORY MASSES

Radu Vasile BUZDUGA[1], Nicolae CONSTANTIN[2], Aurica GOLEANU[3]

The paper aims to study the interactions that lead to the formation of cordierite in refractory masses with its chemical composition. We used a wide range of raw materials consisting of three components: Al_2O_3, MgO, SiO_2, raw materials which differ mainly by their reactivity. Reaction mixtures were heated at 1350°C respectively 1400°C and based on quantitative analysis by X-ray diffraction of the reaction product we prove that the formation of cordierite depends decisively upon the nature of the reactants.

Keywords: cordierite, synthesis, clay, refractory masses

1. Introduction

$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ is the most important ternary compound of the system MgO-Al_2O_3-SiO_2. Its chemical composition, in mass percentage is: MgO - 13,8; Al_2O_3 - 34,8; SiO_2 - 51,4, being situated in the mulit primary crystallization field.[1]

The cordierite presents a complex polymorphism, three forms being acknowledged: the α form named indialit, β- and μ- cordierite. Of these, the indialit is a high temperature stable form and one which can normally be found in nature or that can form in ceramics. β- and μ- cordierite can form just under special conditions.[1]

The indialit is stable until 1460 ^{O}C, the temperature at which it decomposes incongruently with mulit and liquid phase formation, which can develop forsterit, both crystalline phases having much higher thermal expansion coefficients than the indialit from the point of view of the crystalline grid, the cordierite belongs to the ciclosilicat class (being isostructural with beryl $Al_2Be_3[Si_6O_{18}]$). In structure, the cordierite which short christalo-chemical formula is $Mg_2^{[6]}Al_3^{[6]}[S_{i5}Al^{[4]}O^{18}]$, contains coplanar tetrahedral clusters linked in hexagonal of five groups of $[SiO_4]$ and a group $[AlO_4]$. Between the tetrahedral

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[1] PhD student, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: radu_buzduga@yahoo.com

[2] Prof., Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: nctin2014@yahoo.com

[3] PhD eng., Centrul de Cercetare Proiectare si Productie Refractare SA Alba Iulia, Romania, e-mail: ccppr@rdslink.ro

clusters there are octahedral clusters [MgO_6] and [AlO_6] which leave free cavities on the inside of the structural unit. A structural unit is formed by three planes of tetrahedral rings comprising between them two cavities. The thermal behavior of cordierite, its thermal expansion anisotropy, as the possibility of influencing these features find their origin in the structure it has and are of great theoretical and practical importance.[2]

The synthesis of cordierite is possible directly from the oxides and in this sense, the following can be used as raw materials:

- elementary compounds - pure oxides, hydroxides, carbonates;
- double compounds - refractory clays, talc, steatite, sepiolite;
- triple compounds triple - chlorite.

It is advisable to use double or triple compounds, preferably hydrated; the presence of two or three oxides, and the emergence of free connections, resulting in breakage of the network compound during the process of dehydration, guarantee a complete response and a wide range of vitrification.[3]

Along with the nature of raw materials, cordierite formation is strongly influenced by the structural state of the respective reactants, the presence or absence of impurities with mineralizing role, their composition and their specific surface, the size of the area of contact between their grains.

In the ceramics industry we used natural raw materials - talc (soapstone), refractory clays and technical alumina arti. Cordierite is formed according to the following overall reaction:

$$4(3MgO.4SiO_2)+7(Al_2O_3.2SiO_2)+5Al_2O_3 \rightarrow 6(2MgO.2Al_2O_3.5SiO_2) \qquad (1)$$

Basically, though, the reaction does not proceed in total accordance with this scheme. In cordierite ceramic mulit and clinoenstatit are allways present.[4]

These crystalline phases are formed according to the reaction:

$$3MgO.4SiO_2 +2(Al_2O_3.2SiO_2)+3Al_2O_3 \rightarrow 2MgO.2Al_2O_3.5SiO_2+MgOSiO_2+3Al_2O_3.2SiO_2 \qquad (2)$$

2. Experimental work

The characterization of raw materials has been also made in terms of particle size and of their behavior when heated; these results, along with data from the literature were used for this research.

Starting from theoretical considerations, experimental masses were developed using raw materials shown in Table 1, where their chemical composition is indicated.

To calculate the raw material composition in experimental masses we left from the grounds that all blends have cordierite stoichiometry. Using raw materials mentioned in chapter 2.1, there were established four series of compositions, 17 compositions – evidence being developed.

The raw material mixture for each of the experimental masses was wet ground. After drying, samples were made in the form of pills having a diameter of 25 mm, and specimens in the form of rods with dimensions of 65x10x10 m.

The samples were prefired in a laboratory electrical furnace, of kanthal resistance, at a temperature of 1250^{O}C, with a bearing for one hour at maximum temperature. The final heat treatment was performed in a laboratory electric furnace with heating elements of superkanthal at temperatures of 1350^{O}C, respectively 1400^{O}C, with a plateau of one hour at maximum temperature. A third heat treatment applied was made in an industrial furnace chamber with gas for combustion of the refractory, at the temperature of 1350^{O}C, a combustion period of about 20 hours (from cold to cold), the plateau at the maximum temperature is about an hour.[5,6]

Table 1

The chemical composition of the raw material we used

Raw material	Chemical composition [mass percentage]								
	P.C.	SiO_2	TiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O
Refractory clay	14	48,85	0,12	0,68	34,50	0,41	0,31	0,22	0,91
Steatit	5,91	60,12	-	0,61	0,32	0,59	31,59	0,30	0,56
Al_2O_3 - 94%	0,03	0,07	-	0,03	99,48	-	-	0,39	-
Al_2O_3 Gamma	0,80	0,01	-	0,07	98,48	-	-	0,64	-
Amorphous silica	16,14	83,86	-	-	-	-	-	-	-
$Al(OH)_3$	35,84	0,02	-	0,03	63,91	-	-	0,20	-
Quartz-SIKRON SF800	0,26	98,74	-	0,04	0,29	0,01	0,07	0,08	0,51
MgO	12,49	-	-	0,05	-	-	87,46	-	-
$MgCO_3$	53,16	-	-	-	-	1,34	45,50	-	-

On experimental samples of each experimental mass we determined the granulometric composition, we applyed to a sedimentation method using the appliance SediGraph 5100. We took into account the ability of grinding of different raw materials, to highlight possible significant differences between the experimental particle size mixtures, which may essential influence the reactivity of respective masses.[3]

The characterization of experimental masses in terms of their behavior in the thermal treatment was performed by thermal analysis. Thermal curves (ATD and TG) reflect the thermal evolution of these reactive systems, highlighting their chemical and physical transformations characteristic to raw materials as well as neoformation compounds appearance by solid phase reactions or reactions involving liquid phase, as well as formation of liquid phases by interactions of eutectic type between the initial phases or between them and a reaction product previously formed. For all the experimental masses, the ATD curves reveal an exothermic effect with a maximum temperature in the range of 1300-1350 ^{O} C, its position differ from one sample to another and that can be attributed to the formation of cordierite. On the ATD curves of the masses there can be seen also that the exothermic effect due cordierite formation is framed by two endothermic effects that can be attributed to the formation of liquid phases in the respective reagent system. Fig. 1 presents comparative temperatures recorded for the ATD curves for maximum exothermic effect attributed to the cordierite formation, respectively highs endothermic effects attributed to liquid phases that precede (liquid phase I) and follow the formation of cordierite (liquid phase II) for the experimental masses investigated.

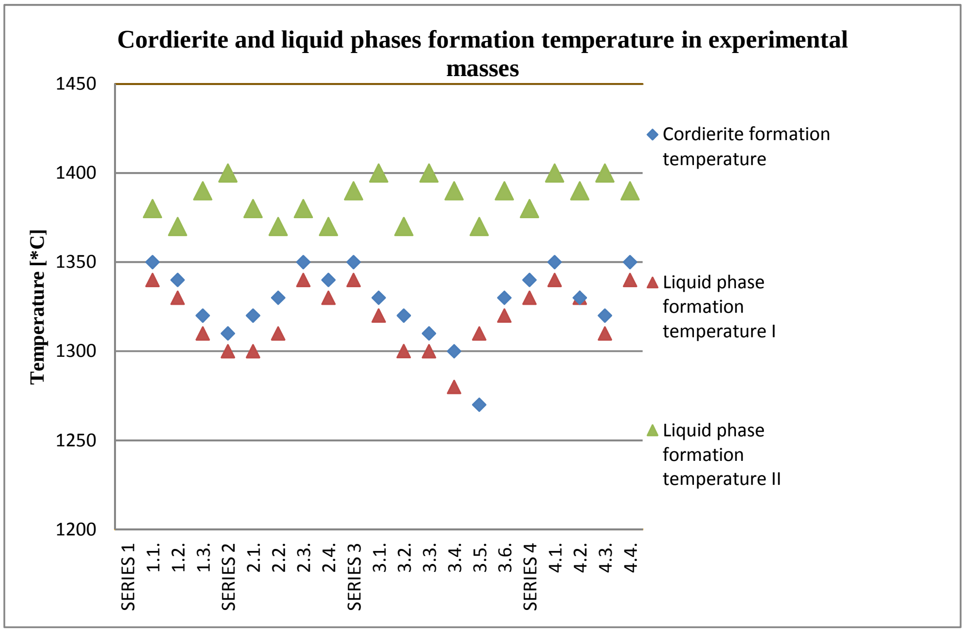

Fig. 1. Cordirite formation in experimental masses

Data provided by thermal analysis performed argue the choice of selection of the heating treatment applied to experimental masses (Fig. 1).

Heat-treated samples were analyzed in terms of mineralogical composition, and the degree of thermal expansion and vitrification.

The mineralogical composition was determined by X-ray diffraction using a Siemens diffractometer Diffrac 500. We used a copper anode and a nickel filter, CuKα radiation being used. For quantitative determination of the phase composition we used the external standard method at a solution based on measurement of attenuation coefficients.

The degree of vitrification of burned samples was determined by measuring the water absorption capacity, apparent porosity and bulk density. Water absorption was done under vacuum, and for the porosity, respectively, the bulk density were performed weighings on the hydrostatic balance [6].

The thermal expansion of burned samples was followed by determining the linear thermal expansion coefficients using the "differential" dilatometer with accessories of silica expansion transmission.

3. Results and discussion

X-ray diffraction spectra of the burned samples, along with data from the literature, allowed the identification of the present crystalline phases. In Fig. 2, the content of cordierite in test samples is shown in comparison.

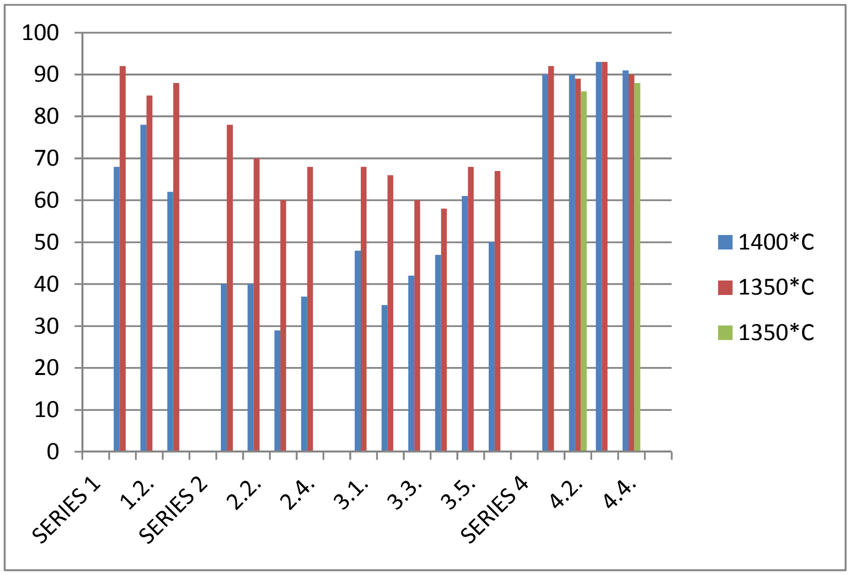

Fig.2. The content of cordierite in burned experimental masses

Given that the extent of vitrification of the burned samples may be a further indication of reactivity of respective masses, they were characterized by measurements of water absorption capacity, apparent porosity and apparent density, microstructural features that define, sufficiently, the compactness of the respective ceramic material.[7]

The values obtained are given in table 2.

Table 2

Values of compactness characteristics of the burned experimental masses

Number of :		The capacity of water absorbtion after burning ar the temperature of: [%]			Apparent porosity, after burning at the temperature of: [%]			Apparent density after burning, aat the temperature of : [g/cm^3]		
series	sample	1350^{O}C	1400^{O}C	1350^{O}C	1350^{O}C	1400^{O}C	1350^{O}C	1350^{O}C	1400^{O}C	1350^{O}C
1	1.1	13.13	12.80	-	24.99	24.37	-	1.91	1.91	-
	1.2	18.14	18.09	-	32.55	31.58	-	1.77	1.74	-
	1.3	18.24	16.99	-	31.81	29.84	-	1.75	1.76	-
2	2.1	20.82	20.44	-	36.05	35.24	-	1.73	1.72	-
	2.2	30.76	32.25	-	45.45	45.70	-	1.48	1.42	-
	2.3	35.11	33.61	-	49.34	46.84	-	1.41	1.39	-
	2.4	41.39	40.44	-	52.78	51.80	-	1.28	1.28	-
3	3.1	26.59	25.59	-	41.32	39.78	-	1.56	1.56	-
	3.2	32.56	32.28	-	46.80	46.11	-	1.44	1.43	-
	3.3	36.64	33.79	-	50.55	46.87	-	1.38	1.39	-
	3.4	37.69	34.03	-	50.18	47.18	-	1.33	1.39	-
	3.5	49.00	46.77	-	56.17	54.39	-	1.15	1.17	-
	3.6	44.26	38.66	-	55.39	50.85	-	1.25	1.32	-
4	4.1	0.71	0.63	-	1.55	1.33	-	2.20	2.16	-
	4.2	5.76	3.31	*0.08*	12.05	6.87	*0.21*	2.09	2.08	*2.55*
	4.3	0.69	2.90	-	1.59	6.18	-	2.32	2.14	-
	4.4	0.73	2.47	*0.05*	1.59	5.19	*0.13*	2.20	2.14	*2.53*

Table 3 presents the values for the linear thermal expansion coefficient determined for two of the experimental masses.

Table 3

The coefficients of linear thermal expansion of the experimental masses

Number of:		Burning temperature [^{O}C]	$\alpha_{20\text{-}100\,^{o}C} \cdot 10^{6}$ [$^{O}C^{-1}$]	$\alpha_{20\text{-}200\,^{o}C} \cdot 10^{6}$ [$^{O}C^{-1}$]	$\alpha_{20\text{-}300\,^{o}C} \cdot 10^{6}$ [$^{O}C^{-1}$]	$\alpha_{20\text{-}400\,^{o}C} \cdot 10^{6}$ [$^{O}C^{-1}$]	$\alpha_{20\text{-}500\,^{o}C} \cdot 10^{6}$ [$^{O}C^{-1}$]	$\alpha_{20\text{-}600\,^{o}C} \cdot 10^{6}$ [$^{O}C^{-1}$]
series	sample							
4	4.1	1400	1.04	1.24	1.44	1.94	2.24	2.54
	4.2	1400	1.04	1.24	1.54	1.94	2.24	2.54

The low values of thermal expansion coefficients can be explained by the presence in their composition, as a dominant crystalline phase, of cordierite, compound with a very low linear thermal expansion coefficient ($\alpha_{20\text{-}1000\,^{o}C}=2\cdot10^{-6}$ $^{O}C^{-1}$) and, in a lower degree, by the porosity of the respective materials.[8]

4. Conclusions

Experimental research results have highlighted the following aspects:

- formation of cordierite in all experimental masses, in the respective burned samples, this being the main fazal component;
- much higher reactivity of the masses containing double hydrated compounds such as clay, steatit, as oposed to those containing elemental compounds, especially oxides – alumina oxides (α-alumina, γ-alumina), silica (β-cuartz, amorphous silica), and respectively, magnesia, hydroxides – aluminum hydroxide, and carbonates – basic magnesium carbonate. This confirms, by experimental data, theoretical hypotesis concerning the influenceof nature and initial structural status of the reagents on the respective reactant systems;
- the positive influence of a rise of thermical treatment temperature upon the the physical and chemical interactions in reaction rpresented by the experimental masses; increasing the duration of heat treatment has also a positive influence on the interactions that lead to the formation of cordierite; gas burning furnace has a favorable influence on the interactions of reagent system, possibly due to circulation and composition of burning gas;
- the variation of reactivity of masses regarding the interactions with liquid phases formation, illustrated by the values determined for the compactness characteristics of the respective masses, is similar to that outlined by the results of thermal and roentgen analysis, the degree of vitrification of the burned masses being considered additional evidence to their reactivity;
- it ows to their presence as dominant crystaline phase, of cordierite and, in a lesser degree to the porosity of the respective materials, being an illustration of the correlation existing between the structure and the properties of a ceramic material.

By the structure of the burned masses and the properties which define the utilization function, some od the experienced masses could be recommended to be used in various technical applicationd: technical ceramics, supports for electrical resistance, catalysts, as well as in other areas where a high resistance to thermal shock can be an advantage.

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