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CERAMIC MATERIALS FROM MAGNESIUM-TREATED CLAYS*

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Thermal expansion characteristics of the crystalline and glassy constituents of ceramic materials are important in determining their physical behavior when the ceramics are placed in service. Refractory materials sometimes fail, largely because stresses derived from differential thermal expansion of their mineral constituents cause ruptures. Cordierite is a magnesium aluminum silicate mineral which has a very low coefficient of thermal expansion. Thus a cordierite body should find wide use in ceramics.

When kaolinite is treated with various magnesium compounds, numerous high-temperature phases develop, depending upon the conditions of treatment and firing. It is believed that the formation of a high-temperature phase can be facilitated if the final crystalline structure is derived from regrouped crystalline units which in turn were derived at a lower temperature from a third crystalline material. For example, in the development of cordierite from magnesium-treated kaolinites, a uniquely crystalline metakaolin phase results following dehydration at 600°C. This combines with MgO at 1000°C. to form spinel. With further increase in temperature spinel combines with cristobalite to give cordierite.

It is not necessary to postulate that at any stage in this sequence the crystalline components were broken down into amorphous constituents which recombined to give the subsequent crystalline phase. Thus the energy requirements in going from one crystalline phase to another, with only moderate shifts in the atomic network, should be appreciably less than if the starting materials were merely mixtures of metallic oxides and hydroxides in the proper proportions to give the desired product. It seemed that cordierite bodies could be produced at lower temperatures if the starting materials were crystalline components such as clay materials.

The high-temperature phases from a variety of kaolinitic clays treated with numerous compounds of magnesium were investigated, chiefly by means of X-ray diffraction. Those formed from mixtures of $MgCO_3$ and a relatively pure kaolinite from Anna, Illinois, are representative and will be discussed here.

Test pieces, 1″ x 1″ x 3″, prepared from mixtures of kaolin and $MgCO_3$ equivalent to 6 and 12 percent MgO, were fired to 1000°, 1100°, 1150°, and 1200°C. The high-temperature phases identified are summarized in table 1. Examination of these data brings out several relationships which seem to indicate something of the effect of various factors on formation of cordierite.

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TABLE 1.—HIGH TEMPERATURE PHASES IDENTIFIED BY X-RAY DIFFRACTION
Anna Kaolin-$MgCO_3$ (equivalent to 12 percent MgO)

	Cord.	*Mullite*	*Crist.*	*Spinel*	*B-qtz.*	*Minor*
1200°C.....	VS*		W			
1150°C.....	S		M	?		
1100°C.....	MS		S	W		
1000°C.....				M	S	Periclase ? Forsterite ?
	Anna Kaolin-$MgCO_3$ (equivalent to 6 percent MgO)					
1200°C.	M	M	S			
1100°C.	MW	M	VS	W		
1000°C.				M		"Gamma alumina" Periclase ?

1. Maximum cordierite is produced at 1200°C. with the addition of $MgCO_3$ in amounts equivalent to 12 percent MgO, with the development of no other aluminum or magnesium phases and with minor amounts of cristobalite.

2. Comparison of samples fired to 1200°C. and containing 6 and 12 percent MgO shows that when the MgO addition is reduced, mullite forms at the expense of cordierite, and cristobalite appears in greater amounts. Raw Anna kaolin containing no MgO fires to mullite and cristobalite only. It would seem that in the magnesium-treated clay, at high temperatures, cordierite and mullite both compete for the alumina constituent, the cordierite taking all the MgO it can utilize. Any alumina left goes into the formation of mullite. If the Al_2O_3 to MgO ratio approximates that of theoretical cordierite, alumina and magnesia are completely used up, with none available for the formation of mullite. This appears to be what happens when the Anna kaolin-$MgCO_3$ mixture (12 percent) is fired to 1200°C., as such a mixture upon dehydration has a chemical composition approximating that of theoretical cordierite (table 2).

3. The decrease in cristobalite which accompanies the increase in cordierite as more magnesium is added to the system suggests that cristobalite is used up in the development of cordierite.

4. Comparison of phases developed at various firing temperatures shows an increase in cordierite with increasing temperature, accompanied by a decrease in cristobalite. The MgO is tied up in phases other than cordierite at the lower temperatures. At 1000° and 1100°C. the phase is spinel.

* VS = Very strong.
S = Strong.
MS = Moderately strong.
M = Moderate.
MW = Moderately weak.
W = Weak.

TABLE 2.—CHEMICAL COMPOSITIONS

	Anna Kaolin 12% MgO (Percent)	*Theoretical Cordierite (Percent)*
SiO_2	49.8	51.4
Al_2O_3	36.4	34.9
MgO	13.8	13.7

Thus the following sequence of events leading to the development of cordierite is suggested. When kaolin is treated with the equivalent of 12-percent MgO (sufficient to give a total chemical composition approximating theoretical cordierite), magnesium and aluminum are tied up in a spinel phase at 1000°C. As the temperature is elevated, cristobalite develops and the spinel becomes unstable, its aluminum-magnesium components combining with cristobalite to form ever-increasing amounts of cordierite. As the temperature increases cordierite continues to increase at the expense of spinel and cristobalite until ultimately at 1200°C. only cordierite and minor amounts of cristobalite are present.

When lesser amounts of MgO are added to the clay, this sequence is modified. At 1000°C. the magnesium is tied up in a poor spinel phase and the alumina in another poorly crystalline phase, probably gamma alumina. As the temperature is raised, the spinel becomes unstable, cristobalite forms, and the two start combining to give cordierite. The gamma alumina is used up in the formation of mullite. As the temperature is raised still higher, more cordierite is formed until at 1200°C. cordierite, mullite, and cristobalite remain.

Thus by varying the treatment of kaolinitic clays with magnesium, a variety of products can be obtained which contain various relative proportions of cordierite, mullite, and cristobalite. Likewise, clays of differing composition show differences in the amounts of high-temperature phases formed. Bodies high in cordierite can be made from common fireclays, which are dominantly kaolinitic but contain appreciable amounts of micaceous clay minerals and quartz. A wide variety of ceramic materials can therefore be developed which exhibit a diversity of properties. Samples containing cordierite as the major constituent are denser and exhibit considerably greater resistance to thermal shock than their non-magnesium-treated equivalents. Their refractoriness is diminished somewhat as MgO is added so that consideration must be given to choosing that property which is most important for each application.

This preliminary laboratory study of such materials can serve as a point of departure for large-scale studies in evaluation of cordierite bodies for commercial use.

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