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KAOLINITE–MULLITE SERIES: FIRING vs. REACTIVE HOT-PRESSING

G. R. BLAIR* and A. C. D. CHAKLADER

Department of Metallurgy, The University of British Columbia, Vancouver 8, Canada

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The effect of an applied pressure on the transformation of metakaolin to spinel has been studied under reactive hot-pressing conditions and the results are compared with the conventionally fired clays. For the experiments both Georgia kaolin and a Canadian fireclay (kaolinitic) were used. The results indicated that the transformation temperature of metakaolin to spinel can be lowered by the application of an external pressure, confirming the earlier work of Carruthers and Wheat. The application of Clapeyron–Clausius equation showed that in order to lower the transformation temperature, the enthalpy change (ΔH) for this transformation has to be positive, contrary to experimental DTA plots, where an exothermic reaction is generally encountered. This anomalous behaviour can be explained, if it is accepted that the exothermic peak at about 900°C in the kaolinite to mullite transformation sequence is due to the crystallization of amorphous silica, as suggested by Nicholson and Fulrath.

The phenomenon of reactive hot-pressing (R.H.P.) has been discussed by several authors [1–5] for a number of materials including kaolinite and other clays. Notably, Carruthers and Scott [4] have discussed the constitutional changes accompanying the R.H.P. of two kaolinites to 1000°. Reactive hot-pressing is essentially a hot-pressing process, in which the pressure is applied when the material undergoes a decomposition reaction or a polymorphic phase change.

The present work was part of a programme of investigation in which the physical properties and mineralogical constituents of reactively hot-pressed clay discs has been carried out [6]. The clays used were hot-pressed to temperatures in excess of 1000° (usually 1050–1150°), and it was thought useful to determine their mineralogical constitution as the very dense discs produced exhibited much improved impact resistance properties over conventionally sintered clays. The results obtained for the reactively hot-pressed specimens are compared with the same clays fired conventionally.

Two clays have been examined in this report:

i) a Georgia kaolin and

ii) a siliceous fireclay from British Columbia, Canada.

These clays after R.H.P. to 1050–1150° undergo changes in colour on subsequent firing in air and specimen density decreases to less than the almost theo-

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* Present address: Koninklijke/Shell Plastics Laboratorium Delft, Postbus 128, Delft, The Netherlands.

retical produced by R.H.P. For example, the densities of fireclay after R.H.P. to 800° and 1100° were 2.06 and 2.56 g/cm^3, respectively, which on subsequent firing to 1500° for 30 hours decreased to 1.84 g/cm^3. Similarly, the Georgia kaolin which after reactive hot-pressing to 1100° had a density of 2.25 g/cm^3, decreased to 1.7 – 1.8 g/cm^3 on subsequent firing at 1500° for 3 hours. Thus we have examined the mineralogical constitution of reactively hot-pressed specimens and subsequently after firing them to 1500°. These results are compared with the relative amounts of constituents in the clays fired to 1500° without any prior R.H.P. step.

Materials

a) A Georgia kaolin having the following composition (in weight percent) was used: 45.8% SiO_2, 38.5% Al_2O_3, 0.7% Fe_2O_3, 1.4% TiO_2 and 13.6% H_2O. The particle size distribution was: 15% below 0.6 μm, 80% between 0.6 and 10 μm, and 5% over 10 μm.

b) The fireclay tested was from Clayburn Harbison Ltd., Abbotsford, B.C., Canada, and had the following composition: 64.5% SiO_2, 23.9% Al_2O_3, 0.83% Fe_2O_3, 0.7% TiO_2, 0.46% CaO, 0.42% MgO, 0.17% Na_2O, 0.07% K_2O and 6.9% loss on ignition. The particle size and mineral content are as follows: between 1 to 10 μm – 30 wt% quartz, 62 wt% kaolin and 8 wt% micaceous and carbonate minerals, and below 1 μm – 85 wt% kaolin and 15 wt% micaceous and carbonate minerals.

Experimental

i) *Specimen fabrication*

Specimens were reactively hot-pressed in a molybdenum die with a graphite liner. Between each molybdenum ram face and the material being pressed a graphite disc was inserted to prevent any reaction with the rams. The die assembly was surrounded by a quartz tube with graphite end-caps and a positive pressure of nitrogen maintained in the enclosed space to prevent oxidation of the molybdenum. Leakage of the blanket gas occurred via small spaces between the rams and the end-caps.

A pressure of 525 kp/cm^2 (51.8 MN/m^2) was applied to the specimen from commencement of heating by means of a hydraulic jack–air multiplier system. Thus a constant pressure could be maintained on the specimen to the final hot-pressing temperature.

Heating was by means of a single-turn induction coil at a rate of 50°/minute. Each specimen was held at the final hot-pressing temperature until compaction, measured on a sensitive dial gauge, ceased. Usually a holding time of about 15°/minutes was sufficient at the maximum temperature used in each run. A fuller description of the apparatus will be published shortly.

After cooling, under zero pressure, to ambient temperature the specimen was extracted and stripped of any adhering graphite. This was followed by wet carborundum grinding of the surfaces to ensure complete graphite removal.

ii) *Specimen examination*

For X-ray diffraction studies and DTA examination, the specimens were crushed and ball-milled using steel balls in a Spex mill. A Philips X-ray diffractometer was used for phase identification and a Du Pont Thermal Analyzer indicated enthalpy change during reactions. All DTA curves were obtained using a heating rate of 15°/minute and a differential scale of 0.008 mV/inch. Initial sample weight was kept constant and no specimen dilution was used.

To establish if R.H.P. produced different phases or differing amounts of phases than resulted from normal firing, a series of clay samples were fired in air to the same temperatures as used for R.H.P. These samples were subsequently ball-milled and examined as described previously.

Finally, the reactively hot-pressed specimens were fired in air to 1500° for 30 hours and the relative amounts of phases present compared with clay straight-fired to this temperature.

Results

a) *DTA*

The DTA curve for raw Georgia kaolin is shown in Fig. 1a. Characteristic peaks at 545° (endothermic) and 1020° (exothermic) were obtained. After R.H.P. to 800° the curve (solid) shown in Fig. 1b was observed. This can be compared to

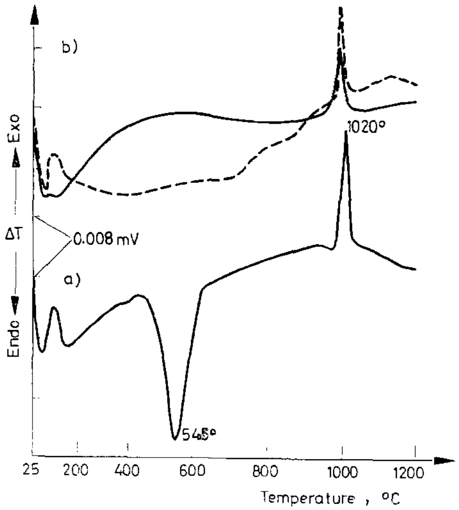

Fig. 1. DTA plots in air of Georgia kaolin. (a) Raw clay; (b) clay RHP to 800° (solid), clay fired to 800° (broken)

the curve obtained for a specimen fired to the same temperature without the application of pressure (broken curve). It can be seen that the exothermic peak for the R.H.P. specimen is smaller than for the fired material after heating to the same temperature.

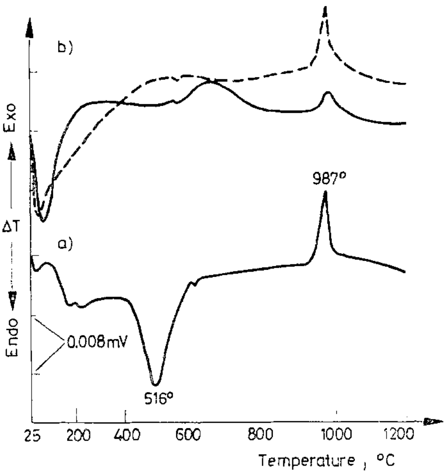

Fig. 2. DTA plots in air of fireclay (origin, B.C. Canada). (a) Raw clay; (b) clay RHP to 800° (solid), clay fired to 800° (broken)

The raw fireclay DTA curve in Fig. 2a shows an endothermic peak at 516° and an exothermic peak at 987° as well as the small endothermic peak accompanying the $\alpha \rightarrow \beta$ quartz inversion at 573°. As in the case of the Georgia kaolin the intensity of the exothermic peak is smaller for the R.H.P. specimen than for the fired specimen after treatment to 800° (Fig. 2b). The height of the exothermic peak for the fired material is almost the same as for the raw clay. Only the quartz transformation peak was observed for fireclay reactively hot-pressed or fired to 1100°.

b) *X-ray diffraction*

The X-ray diffraction pattern for the Georgia kaolin corresponded to kaolinite having a triclinic structure as recorded by Brindley and Robinson [7].

After heating to 800°, fired material showed weak metakaolinite peaks only, whereas the reactively hot-pressed material also showed some very weak cubic spinel peaks. The amount of mullite in the reactively hot-pressed kaolin after heating to 1100° was greater than that produced by straight firing.

Subsequent firing of the specimens, which had been initially reactively hot-pressed to 800 and 1100°, to 1500° for 30 hours produced strong mullite and very strong α-cristobalite peaks. The relative amounts of these phases differed from the peak intensities of material fired to the same temperature without being previously reactively hot-pressed. The normalised intensities for the strongest peaks for mullite and α-cristobalite after the three firing treatments are shown in Table 1.

Since there was free quartz present in the fireclay very strong peaks were obtained in X-ray diffraction patterns for this constituent. These peaks will be ignored except where their consideration is of importance.

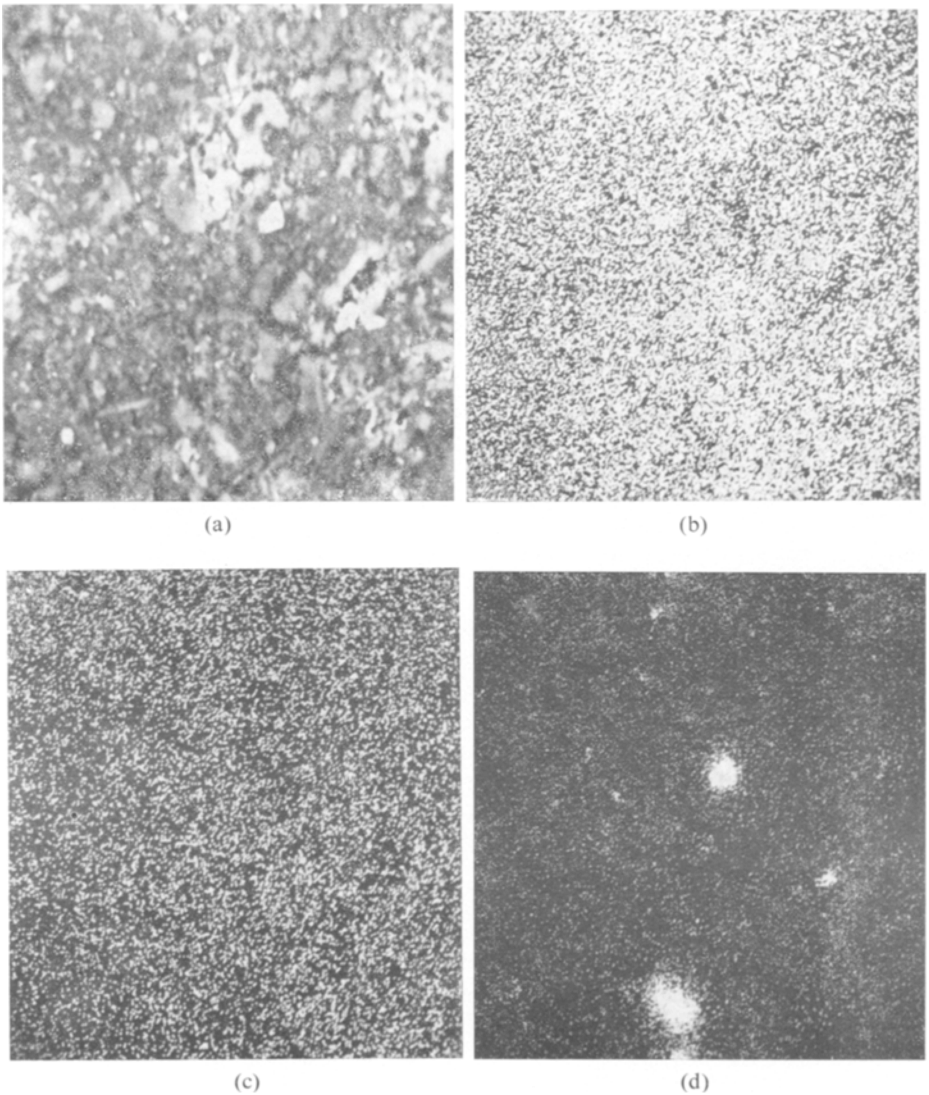

Fig. 3. Reactively hot-pressed Georgia kaolin (1100°). (a) Absorbed electron image; (b) Si distribution; (c) Al distribution; (d) Ti distribution

Table 1

Normalised intensities of mullite and α-cristobalite in Georgia kaolin fired to 1500° for 30 hours

Pre-treatment	Constituent	*d*-spacing	Intensity
none	mullite	3.39	60
	α-cristobalite	4.05	100
R.H.P. to 800°	mullite	3.39	80
	α-cristobalite	4.05	100
R.H.P. to 1100°	mullite	3.39	100
	α-cristobalite	4.05	80

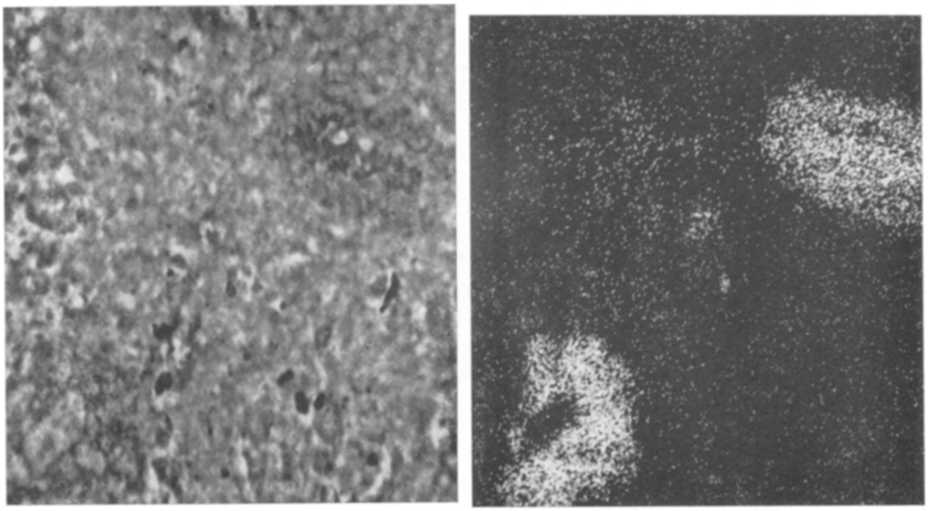
(a) (b)

Fig. 4. Reactively hot-pressed (B.C.) fireclay (1100°). (a) Absorbed electron image; (b) Fe distribution

Table 2

Normalised intensities of mullite and α-cristobalite in fireclay fired to 1500° for hours

Pre-treatment	Constituent	*d*-spacing	Intensity
none	mullite	3.39	60
	α-cristobalite	4.05	100
R.H.P. to 1100°	mullite	3.39	100
	α-cristobalite	4.05	100

In fireclay fired to 800° the presence of cubic spinel was barely discernible, whereas identifiable amounts of this constituent were detected in fireclay reactively hot-pressed at the same temperature. Similarly, greater amounts of mullite were present after reactively hot-pressing to 1100° than by firing to this temperature.

Subsequently firing material, previously R.H.P. to 1100°, for 30 hours at 1500° produced very strong mullite and α-cristobalite peaks. The relative amounts of these constituents differed from that produced by firing alone (see Table 2).

c) *Electron microprobe studies*

The microstructure and distribution of the elements present in the two clays was observed using a JEOL electron microprobe. The Georgia kaolin R.H.P. to 1100° showed no porosity (Fig. 3a), and a homogeneous distribution of SiO_2 (shown as Si) and Al_2O_3 (as Al) was observed (Fig. 3b and 3c). However, small concentrated areas of TiO_2 were noted (Fig. 3d). Similarly low or zero porosity was found for reactively hot-pressed fireclay confirming that this hot-pressing technique produces specimens which are almost theoretically dense (see Fig. 4a). In this material areas of concentration of Fe_2O_3 (as Fe) were observed (Fig. 4b).

Discussion

I. *Reactive hot-pressing to 800°*

Georgia kaolin reactively hot-pressed or fired to 800° has a very weak X-ray diffraction pattern. This is similar to the results obtained by Brindley and Nakahira [8] during their investigation of single crystals of kaolinite. However, after the clay had been reactively hot-pressed to this temperature, the presence of cubic spinel was evident. Brindley and Nakahira state that this phase is only metastable over the temperature range 925–1075° but it has been detected at 850° [9]. Its presence after treatment at 800° suggests that reactive hot-pressing has induced the formation of the spinel phase at a lower temperature than found on normal firing (without the application of pressure).

Although the detection of peaks in the fireclay was somewhat masked by the strong α-quartz peaks, the same phenomenon was found, i.e. the formation of cubic spinel at 800° after reactive hot-pressing.

Our results for kaolinite reactively hot-pressed to 800° are in agreement with those of Carruthers and Wheat [10]. They pressed kaolinite at pressures exceeding 784 kp/cm^2 (77 MN/m^2) to 750° and found phases which at normal pressure are not formed below 1000°. Also Wheat [11] has shown that this phenomenon causes the strong exothermic peak to be eliminated. In our work, which has been carried out at lower hot-pressing pressures, this peak is still present in clays pressed to 800° but of a smaller magnitude than for raw clay or clay fired to 800° without the application of pressure.

A comparison of the phases identified by Carruthers and Scott [4] after reactively hot-pressing two kaolinites shows good agreement with the present results, i.e. after hot-pressing to 750° using pressures up to 940 kp/cm^2 (92.6 MN/m^2), they only detected metakaolin, but at 1000°, cubic spinel and weak mullite were detected. However, in this pressure range [up to 940 kp/cm^2 (92.6 MN/m^2)], the amount of mullite developed in a well-ordered clay at 1000° was very much less than would be formed at atmospheric pressure. This is contrary to our findings for kaolinite.

II. *Temperatures up to 1500°*

The proportions of the phases produced after firing material to 1500° have been estimated from the intensities of the strongest peaks for each phase. For Georgia kaolin the ratio of mullite to α-cristobalite for normally fired material was 0.6, whereas the same ratio was 0.8 and 1.25 for clay initially reactively hot-pressed to 800 and 1100°, respectively, i.e. the higher the reactive hot-pressing temperature the greater the amount of mullite formed on subsequent firing.

Similarly, the relative amounts of mullite and α-cristobalite differed after firing the previously reactive hot-pressed and straight fired fireclay to 1500° for 30 hours. For materials conventionally fired the ratio of mullite to α-cristobalite was 0.6, whereas for materials initially hot-pressed to 1100° the ratio was 1.0. Thus, although the fireclay contained a significant amount of free quartz there has been a stabilization of mullite phase.

III. *Effect of pressure on the metakaolin to spinel transformation*

From the foregoing, it is apparent that the spinel phase was formed at a lower temperature under reactive hot-pressing conditions than is generally observed during normal firing clays. The only difference between these two treatments is that during reactive hot pressing an external pressure was present during the reaction (dehydroxylation reaction or crystallographic transformation). The metakaolin to spinel transformation generally takes place in the temperature range 925–1075°. However, in the present case, spinel was encountered at 800°, indicating that the metakaolin to spinel transformation occurred at or below 800°, under the influence of an external pressure of 525 kp/cm^2 (51.8 MN/m^2).

The effect of pressure on the phase-transformation temperature can be quantitatively estimated by the Clapeyron–Clausius equation for a one component–two phase system. In order to apply this equation to a transformation, such as metakaolin to spinel, it has been assumed that during this transformation, the excess SiO_2 (i.e. exsolved SiO_2) was present in the spinel lattice, i.e. the spinel phase is supersaturated with SiO_2.

The metakaolin to spinel transformation can be written as follows:

$$\underset{\text{(metakaolin)}}{Si_4Al_4O_{14}} \rightarrow \underset{\text{(spinel)}}{Si_3Al_4O_{12}} + \underset{\text{(supersaturated)}}{SiO_2} \qquad (1)$$

In differential form, the Clapeyron–Clausius equation is:

$$\frac{\mathrm{d}T}{\mathrm{d}P} = \frac{T\Delta V}{\Delta H} \tag{2}$$

Provided that the change of molar volume (ΔV), and the change in enthalpy (ΔH), are not sensitive functions of pressure, Eq. (2) can be integrated to:

$$\ln \frac{T}{T_0} = \frac{\Delta V_0}{\Delta H_0} (P - P_0) \tag{3}$$

For a positive increment in pressure [i.e. $(P - P_0) > 0$] one can see immediately that if ΔV_0 and ΔH_0 have the same sign $T > T_0$ and if they are of opposite sign $T < T_0$.

The effect of the applied pressure on the temperature of metakaolin to spinel transformation can be quantitatively evaluated, provided the change in molar volume and the enthalpy for the reaction are known. In the case of metakaolin to spinel transformation, the ΔH has been reported [12] to be in the range -5 to -15.5 kcal/mole (ΔH is negative). However, the latest work by Nicholson and Fulrath [13] suggests that for well crystallized and pure kaolinite, the ΔH associated with this transformation is -9 kcal/mole.

The molar volumes for the metakaolin and the spinel phases are calculated as follows. The unit cell dimensions of metakaolin were originally reported by Brindley and Nakahira [8] to be 5.1 × 8.9 × 12.6 Å. This was subsequently corrected by Freund [14] as 5.1 × 8.9 × 13.7 Å ($C_0 = 2 \times d_{001}$). Using the formula for the unit cell of metakaolin as $Si_8Al_8O_{28}$, the theoretically calculated density is 2.37 g/cm^3. This density value is very close to the value of 2.36 g/cm^3 reported by Range et al. [15] for kaolinite just after decomposition at 550° (i.e. for metakaolin). However, this density value is higher than the theoretically calculated value of Freund [14] in which he assumed no dimensional change in C_0 of kaolinite after dehydroxylation. Using the unit cell dimension of metakaolin as reported by Freund and 2.37 g/cm^3 as the true density, the molar volume of metakaolin is 374.367 cm^3/g atom.

The unit cell dimension of the spinel (alumino-silicate spinel) was reported by Brindley and Nakahira [8] to be 7.88 Å (cubic-cell edge length) and having the chemical formula of $Si_8Al_{102/3}O_{32}$. The theoretical density of spinel has been calculated to be 3.265 g/cm^3. If it is assumed, however, that all excess SiO_2 is in the spinel lattice in a supersaturated state, then the formula of metakaolin $Si_8Al_8O_{28}$ can be used for the calculation of the density of spinel (with supersaturated SiO_2) and this gives a value of 3.007 g/cm^3. Comparing the unit cell volume of metakaolin (621.84 Å^3) with that of spinel (490.42 Å^3), it is apparent that there is a reduction in volume of about 21 %. This is in agreement with the observation of Freund [14], who reported that about 20 vol. % of lattice vacancies disappeared during this transformation at 950–970°. The molar volume of spinel is then 295.23 cm^3/g atom, with supersaturated SiO_2 (and 295.28 cm^3/g atom, without excess SiO_2 in the lattice). Thus the change in molar volume (ΔV) is -79.13 cm^3/g atom. Although this value for the change in molar volume during this transformation may not be exact there is no denying that the change in molar volume is negative. This can also be easily seen from the change in true density associated with the metakaolin to spinel transformation.

From the above, it follows that since $(P - P_0)$ is a positive number and as both ΔV and ΔH are negative, the application of an external pressure (P) should increase the transformation temperature, which is exactly opposite to that experimentally observed, where the high temperature phase was encountered at a lower temperature than normal. This contradiction between the prediction and the experimental observation can only be resolved if it is considered that ΔH for the reaction (Eq. 1) is positive, as ΔV is definitely negative. Recently, Nicholson and Fulrath [13] have suggested that the experimentally determined negative ΔH of -9 kcal/mole during the metakaolin to spinel transformation is not for this reaction but for the crystallization of amorphous SiO_2 to β-quartz. It is proposed here that there exists a positive enthalpy change ($+\Delta H$) for the metakaolin to spinel transformation which may be smaller in magnitude than the negative enthalpy change for the crystallization of SiO_2 and thus may be obscured during experimental measurements. In fact, it is possible that experimentally determined negative enthalpy change -9 kcal/mole is the sum of the following simultaneous reactions:

Reaction (1): Metakaolin $\xrightarrow{\Delta H_1}$ spinel with supersaturated SiO_2

Reaction (2): Spinel S · $SiO_2 \xrightarrow{\Delta H_2}$ spinel + SiO_2 amorphous

Reaction (3): SiO_2 amorphous $\xrightarrow{\Delta H_3}$ SiO_2 crystalline.

All these reactions may occur simultaneously, but detailed experimental proof is lacking at present.

With the above considerations, an attempt has been made to calculate the extent of ΔH (+ ve) for the metakaolin to spinel transformation, using the Clapeyron–Clausius equation (Eq. 3). It is not known at present what would be the lowest temperature and pressure at which the transformation of metakaolin to spinel can be accomplished. In the present investigation it has been shown that spinel can be formed at 800° under 525 kp/cm^2 (51.8 MN/m^2). Using these values of temperature and pressure, $\Delta V = -79.13$ cm^3/g-atom and Eq. (3), the ΔH has been calculated to be about $+7.5$ kcal/mole, which is smaller than the value of $-\Delta H$, calorimetrically measured by Nicholson and Fulrath. However, it should be mentioned here that without further work on the temperature and pressure diagram of metakaolin–spinel transition, the quantitative evaluation of ΔH for this transformation cannot be made.

It is possible that this positive enthalpy change ($+\Delta H$) of 7.5 kcal/mole for the metakaolin to spinel is being swamped by the enthalpy change during the crystallization of amorphous silica and thus could not be detected by any experimental technique. It is likely that the total heat release during crystallization is about -16 kcal/mole, which is the upper limit of the experimentally determined enthalpy change observed so far [16]. On the other hand, if the exsolution of SiO_2 from the metakaolin lattice is a slow, gradual and continuous process, and takes place over a large range of temperature, then the effect of $+7.5$ kcal/mole from this transformation will not be reflected on the heat release for the crystallization of SiO_2. It should be emphasized here that the application of an external pressure will raise the transformation temperature of SiO_2 amorphous $\rightarrow$ SiO_2 crystalline as it has a negative ΔH and negative ΔV for this transformation.

It is interesting to note in this respect that several investigators [12e, 14, 17] have reported an endothermic reaction preceding the strong exothermic reaction. This also can be seen in Fig. 1, in the case of Georgia kaolin, but this endothermic peak was never encountered in the case of fireclays, indicating that lattice distortion or defects might have eliminated this endothermic peak in the latter case.

From the above analysis, it can be inferred that the enthalpy change for the metakaolin to spinel transformation is positive and small. It also substantiates the conclusion of Nicholson and Fulrath [13] that the exothermic reaction encountered in a data plot of kaolinite is due to the heat release associated with the crystallization of SiO_2 from the amorphous state.

Conclusions

A study of the effect of an external pressure on the metakaolin to spinel transformation indicated that this transformation temperature can be lowered. The application of the Clapeyron–Clausius equation showed that in order to lower the temperature of transformation, the enthalpy change (ΔH) for this transformation has to be positive. The exothermic reaction (i.e. $-\Delta H$) above 900° generally observed in a DTA plot during the transformation of kaolinite to mullite, may be due to the crystallization of amorphous silica, as recently proposed by Nicholson and Fulrath. The formation of both mullite and spinel at a lower temperature under reactive hot-pressing conditions than that generally obtained during heating indicates that the enthalpy changes for the transformation of metakaolin to spinel and spinel to mullite are both positive.

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Résumé — Etude de l'influence de la pression exercée à chaud sur la transformation du métakaolin en spinelle et comparaison des résultats avec ceux obtenus avec les argiles calcinées de manière conventionnelle. Les expériences ont été pratiquées sur un kaolin de Géorgie et sur une argile kaolinitique du Canada. Les résultats montrent que le fait d'exercer une pression extérieure abaisse d'une manière importante la température de la transformation du métakaolin en spinelle. La variation d'enthalpie correspondante a été calculée à l'aide de l'équation de Clausius—Clapeyron. On l'a calculé positif, cependant les pics ATD montrent une réaction exothermique. On peut expliquer ce comportement anomalistique par la suggestion de Nicholson et Fulrath, selon laquelle le pic exothermique de 900° dans la transformation kaolinite/mullite est due à la cristallisation de l'oxyde de silice amorphe.

Zusammenfassung — Der Einfluß eines geeigneten Druckes auf die Umwandlung von Metakaolin in Spinell wurde unter den Bedingungen des reaktiven Warmpressens untersucht und die Resultate mit den für konventionell gebrannten Ton erhaltenen verglichen. Die Versuche erfolgten mit einem Kaolin aus Georgia und einer Tonart aus Kanada. Die Ergebnisse zeigen, daß die Übergangstemperaturen Metakaolin—Spinell durch Anwendung eines äußeren Druckes erheblich vermindert werden können. Mit Hilfe der Clausius—Clapeyronschen Gleichung wurde für die Umwandlung eine positive Enthalpieänderung errechnet, hingegen deuteten die experimentellen DTA Spitzen eine exothermische Reaktion an. Dieses anomalische Verhalten läßt sich durch die Annahme von Nicholson und Fulrath erklären, nach der die exothermische Spitze bei 900° beim Kaolinite—Mullit Übergang der Kristallisation des amorphen Siliziumdioxyds zuzuschreiben ist.

Резюме — Изучено влияние давления на превращение метакаолина в шпинель в условиях горячего реакционного прессования и результаты сравнены с данными, полученными для случая обычных обожженных глин. Эксперименты проведены с каолином из Георгии и огнеупорной глиной из Канады. Результаты показали, что температуру превращения метакаолина в шпинель можно значительно уменьшить использованием внешнего давления. Положительное изменение энтальпии ($+\Delta H$) рассчитано для перехода метакаолина в шпинель по уравнению Клапейрона-Клаузиуса.