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STUDY OF SOLID-PHASE TRANSFORMATIONS DURING MECHANOCHEMICAL AND THERMAL TREATMENT OF ALUMINOSILICATE SYSTEMS USING THERMAL ANALYSIS

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ABSTRACT

Effect of mechanochemical activation of the hydrargillite-silica mixture upon the sequence of solid-phase transformations during its further thermal treatment has been investigated. The similarity of solid-phase transformations in the activated mixture and a number of other aluminosilicate systems has been found.

INTRODUCTION

Development of novel wasteless technologies for the synthesis of high-temperature supports and catalysts, ceramic materials and refractories (based on complex oxide compounds), as well as improvement of their quality have acquired ever increasing interest nowadays. The most promising way in solving these problems is mechanochemical treatment of low-active compounds aimed at increasing their reactivity. To obtain the purpose product with the given properties, the knowledge of mechanism of solid-phase transformations during its formation is necessary. One of the most informative ways for the investigation of the above transformations is a complex thermal analysis.

In the present work the mechanism of solid-phase transformations of aluminosilicate systems is studied. The object of investigation is the hydrargillite (HG) and silica (SC) mixture with the ratio $Al_2O_3:SiO_2=1:2$, which has been subjected to mechanochemical activation. The $Al_2O_3:SiO_2$ ratio was chosen to study the similarity of solid-phase transformations in kaolinite and in the activated mixture (HG+SC)*.

MEASURING METHODS

The complex thermal analysis of the samples was performed on a F.Paulik-J.Paulik-L.Erday installation at the rate of heating of 7.5 K/min up to 1773 K.

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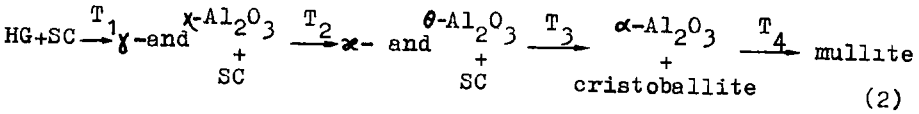
The X-ray analysis was carried out on a "DRON-2" diffractometer using a CuK_α-irradiation, monochromatized with a graphite monochromator on a reflected beam.

RESULTS AND DISCUSSION

During activation of the HG+SC mixture amorphization of the mixture with retention of water content in the initial mixture (composition $Al_2O_3 \cdot 2SiO_2 \cdot 3{,}5H_2O$) occurs. The DTA curve of the activated $(HG+SC)^*$ mixture has one endothermic (a maximum at 473 K) and two exothermic (1253 and 1553 K) effects. The DTA curve of the mechanical mixture prepared from separately activated hydrargillite HG* and silica SC*, differs from that of the activated $(HG+SC)^*$ mixture. These data indicate that even at the step of mechanochemical activation, the components interact producing amorphous aluminosilicate. A broad endoeffect (343÷773 K) with a maximum at 473 K appearing on the DTA curve of the activated $(HG+SC)^*$ mixture results from complete dehydration of the amorphous aluminosilicate. The exoeffect with a maximum at 1253 K is revealed in a narrow temperature range 1233÷1273 K and is very intensive. It is caused by crystallization of the amorphous aluminosilicate to the phase with the spinel structure. The crystallization of mullite is accompanied by a low-intensive exoeffect at 1553 K. The main steps of solid-phase transformations of the activated $(HG+SC)^*$ mixture may be represented as follows:

$$(HG+SC)^* \xrightarrow{T_1^*} \begin{array}{l}\text{unhydrous}\\ \text{amorphous}\\ \text{aluminosilicate}\end{array} \xrightarrow{T_2^*} \text{spinel} \xrightarrow{T_3^*} \text{mullite} \qquad (1)$$

For comparison, solid-phase transformations in the GH+SC mixture, that was not activated mechanochemically, were examined too. The DTA, DTG and TG curves of the unactivated GH+SC mixture result from an additive superposition of the corresponding curves for individual components. This indicates that the components in the unactivated mixture undergo the same phase transformations as individual components and do not noticeably affect each other. Mullite from the unactivated mixture is formed via a more multi-step route than that from the activated mixture:



$$HG+SC \xrightarrow{T_1} \gamma\text{-and}\ \underset{SC}{\underset{+}{\chi\text{-}Al_2O_3}} \xrightarrow{T_2} \varkappa\text{- and}\ \underset{SC}{\underset{+}{\theta\text{-}Al_2O_3}} \xrightarrow{T_3} \underset{\text{cristoballite}}{\underset{+}{\alpha\text{-}Al_2O_3}} \xrightarrow{T_4} \text{mullite} \qquad (2)$$

As seen from the comparison of sequence (1) and (2), the mechanochemical activation leads to a change in the mechanism of solid-phase transformations.

According to the literature data, sequence (1) is observed also upon thermotreatment of coprecipitated aluminosilicate gels [1], kaolinite [2] and kaolinite subjected to mechanochemical activation [3]. Like in the case of activated (GH+SC)[*] mixtures, the phase with the spinel structure is formed from the above samples via the formation of unhydrous amorphous aluminosilicate. The DTA curves of said samples [1-3] are characterized by the presence of a broad endothermic effect, attributed to the complete dehydration of aluminosilicate, by a narrow intensive exothermic effect with a maximum at 1253 K and a low-intensive exothermic effect with a maximum in the range of 1553 K.

CONCLUSIONS

Thus, the complex thermal analysis has indicated the similarity of the nature of solid-phase transformations that take place during thermal treatment of such systems as coprecipitated aluminosilicate gels, unactivated kaolinite, mechanochemically activated kaolinite and activated hydrargillite-silica mixture. Mechanochemical activation of kaolinite does not affect the sequence of its solid-phase transformations during subsequent thermal treatment, whereas this effect is quite essential for the mechanical hydrargillite-silica mixture.

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