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The solubility of nanocrystalline mechanocomposites with biologically active substances in the aqueous medium

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Debonding of succinic and tartaric anions from mechanocomposites of these acids with talc and kaolinite and their transition into solution are investigated. It is found that under the experimental conditions, the talc-based composites get dissolved almost completely within 1 min. The dissolution of the composites of succinic acid and kaolinite occurs gradually within ∼20 min; the rate of dissolution is depending on activation time. The time necessary for dissolution of mechanocomposites of tartaric acid both with talc and with kaolinite is 1 min. Probable reasons of differences in the solubility of the composites are discussed.

1. Introduction

During the joint mechanical activation of natural layered silicates with organic acids, as a result of the mechanochemical reaction, the basic active centers of silicates are neutralized by the protons of acids with the formation of highly homogenous nano-sized mechanocomposites in which the anions of acids are chemically bound with the metal ions of silicates [1, 2]. These composites are salts of the acids from the structural viewpoint. Because of that, the medical products of succinic, salicylic, ascorbic and other biologically active acids prepared by mechanochemical methods are expected to not irritate the mucous coat of stomach; the irritation would be especially dangerous for persons with elevated acidity of gastric juice or with stomach ulcer. From this point of view, the mechanochemical method of obtaining medicines is very promising. In addition, fine disperse state and homogeneity of mechanocomposites can help solving the problem of bio availability of medicines, since this parameter is limited by the rate of dissolution, depending on particle size and the structure of the substance.

The aim of the present work is to investigate the dissolution of nano-sized mechanocomposites of dicarboxylic acids with talc and kaolinite. Here and below, dissolution of mechanocomposites means the process of debonding of acid anions, which are chemically bound in the mechanocomposite, from the carrier and their transition into solution.

2. Experimental

Mechanocomposites of succinic $(COOH)_2(CH_2)_2$ and tartaric $(CH_2)_2(OH)_2(COOH)_2$ acids obtained by the joint activation with layered silicates—talc $Mg_3(Si_4O_{10})(OH)_2$ and kaolinite $Al_2(Si_2O_5)(OH)_4$ were investigated. Molar ratios (MR) of the components in the composites were: silicate:acid = 1:1. Nanocrystalline mechanocomposites were prepared and their subsequent disintegration was carried out in an AGO-2 planetary ball mill.

In order to investigate the solubility, 0.4 g of a mechanocomposite was placed into 25 ml of an aqueous solution of hydrochloric acid ($pH \approx 1$) at room temperature. The mixture was stirred continuously (the frequency of rotation of the magnetic mixer was ∼80 rpm). According to the calculation data, 0.4 g of the talc-based mechanocomposite contains 0.095 g of succinic acid or 0.12 g of tartaric acid. 0.4 g of kaolinite-based mechanocomposite contains 0.61 g of succinic acid or 0.15 g of tartaric acid. Dissolution was performed within a definite time interval $1.0 \leq \tau_d \leq 120$ min. After that, the sample was centrifuged; concentration (%) of acid anions was determined in the aqueous fraction by means of voltammetry [3].

Relative error of the determination of concentration of acids does not exceed ±7%. No effect of talc and kaolinite on the signal height has been detected. Specific surface of the composites was determined by means of argon adsorption/desorption at $T = 77$ K from the powder surface.

3. Results and discussion

The dynamics of the transition of acid anions from composite into solution is shown in Figs 1 and 2 ([A] is concentration of acid anions, %; τ_d is dissolution time). It follows from Fig. 1 that in the case of talc-based

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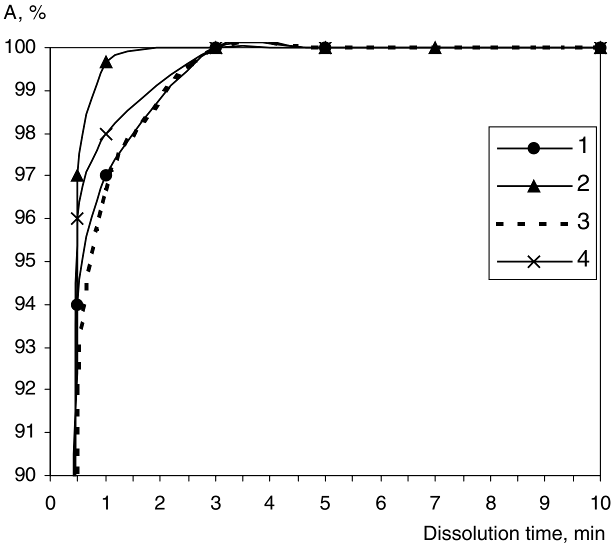

Figure 1 The dynamics of dissolution of talc-based mechanocomposites of succinic (3, 4) and tartaric (1, 2) acids with various activation time: 1 – 1 min; 2 – 3 min, 3 – 5 min, 4 – 7 min.

mechanocomposites the acid anions get detached and pass into solution almost completely within $\tau_s \approx 1$ min, both for the samples containing free acid and for the samples containing no free acid, i.e., taken before or immediately after the mechanochemical reaction [2]; activation time was $\tau_a \leq 5$ min and $\tau_a \leq 3$ min for succinic and tartaric acid, respectively.

Quite a different phenomenon is observed for kaolinite-based mechanocomposites. In the case of composites of succinic acid sampled at the initial stage of mechanochemical interaction, at $\tau_a \leq 1$ min, containing substantial amount of the unreacted acid [2], the anions of the free acid pass into solution almost from the beginning of dissolution process (Fig. 2, curve 1). With a decrease in the concentration of unbound acid in the samples (i.e., with an increase in activation time), the transition of the ions into solution slows down. For samples containing no free acid (i.e., sampled after the completion of the mechanochemical reaction) and further activated ($\tau_a = 5$ and 7 min), the rate of the transition of acid anions into solution depends both on

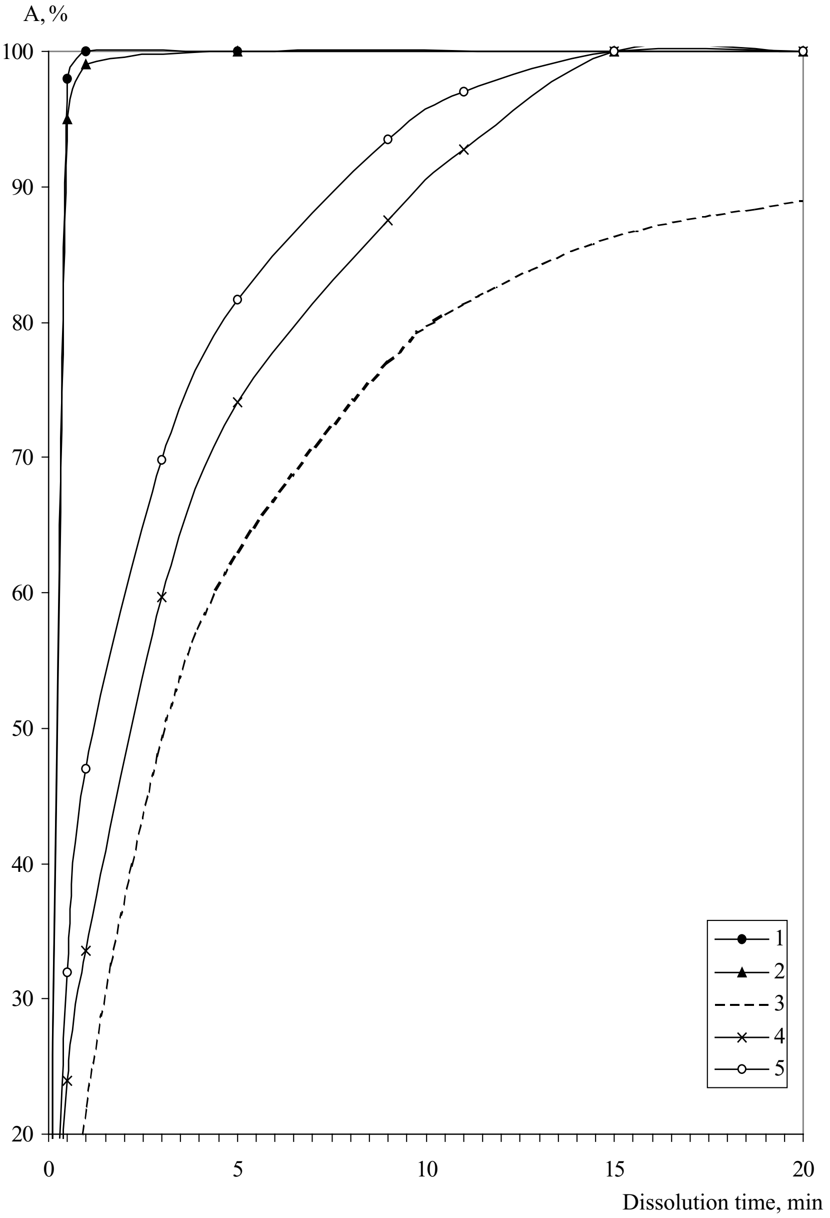

Figure 2 The dynamics of dissolution of kaolinite-based mechanocomposites succinic (1, 3–5) tartaric (1, 2) acid with various activation time: 1 – 1 min, 2 – 3 min, 3 – 5 min, 4 – 7 min, 5 – 9 min.

dissolution time and on activation time (Fig. 2, curves 3, 5). The disperse state (specific surface) of the samples increases during activation [3]. It reaches its maximum after the completion of the mechanochemical reaction ($\tau_a = 5$ min). However, these samples exhibit the lowest solubility (Fig. 2, curve 3). With longer activation time, the solubility of samples increases (Fig. 2, curves 4, 5). The observed decrease in specific surface (Table I) is likely to be connected with the secondary aggregation which does not affect the solubility, because the dissolution was performed under continuous agitation.

While the $[A] = f(\tau_d)$ dependencies for the talc-based mechanocomposites of succinic and tartaric acids are almost identical (Fig. 1), they are substantially different from each other for kaolinite-based mechanocomposites (Fig. 2). For the samples taken before completion and immediately after completion of the mechanochemical interaction ($\tau_a \leq 3$ min), the tartaric anions pass into solution almost completely within 1 min, similarly to the case of talc-based mechanocomposites.

The character of dissolution of the talc- and kaolinite-based mechanocomposites of succinic and tartaric acids is due both to the features of (i) the crystal structure of silicates determining the structure and composition of mechanocomposites, and (ii) structure and properties of acids.

Mechanocomposites can be conventionally represented as the compounds:

talc–succinic acid: $[Mg_3(Si_4O_{10})]^{2+} \cdot (COO^-)_2R$;
talc–tartaric acid: $[Mg_3(Si_4O_{10})]^{2+} \cdot (COO^-)_2(OH)_2R$;
kaolinite–succinic acid: $[2Al_2(Si_2O_5)(OH)_3]^{2+} \cdot (COO^-)_2R$;
kaolinite–tartaric acid: $[2Al_2(Si_2O_5)(OH)_3]^{2+} \cdot (COO^-)_2(OH)_2R$.

It may be assumed that the anions of succinic and tartaric acids in talc-based composites are bound with the cation mainly by electrostatic forces and can be easily extracted into the low acidic solution (within 1 min) dissociating almost completely according to the strong electrolyte type. In kaolinite-based composites of succinic acid, the bonding strength of the bond between cation and anion can be increased due to the formation of hydrogen bonds between the OH groups of kaolinite and acid anions. Because of this, anions pass into solution slower; they do it gradually within 20 min. The presence of hydroxy groups in the structure of tartaric acid is likely to prevent the formation of hydrogen bonds with kaolinite. As a result, the anions of tartaric acid pass into solution easily, similarly to talc-based composites. This assumption is confirmed by the fact that acid anions pass into solution within 1 min independently of activation time in the presence of unreacted acid in composite (MR of kaolinite:tartaric acid = 1:2).

4. Conclusions

Investigations of the dynamics of dissolution of the mechanocomposites of succinic and tartaric acids showed that the debonding of acid anions and their transition into solution from talc-based composites occurs within approximately 1 min under the experimental conditions involved. Such a process is slower for kaolinite-based composites of succinic acid; it completes within ∼20 min. Tartaric acid from both talc- and kaolinite-based composites dissolves within 1 min.

The established regularities of dissolution of the composites of succinic and tartaric acids are determined by the strength of anion bonding to carrier. These bonds are stronger in the composites of succinic acid with kaolinite due to the formation of additional hydrogen bonds between the acid anion and hydroxy groups of kaolinite. The presence of hydroxy groups in the structure of tartaric acid prevents the formation of similar hydrogen bonds in kaolinite-based composites, therefore, dissolution occurs within 1 min, similarly to the case of talc-based composites.

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