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THERMAL DECOMPOSITION OF MECHANICALLY ACTIVATED ARSENOPYRITE

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Abstract

The changes in specific surface area and structure disorder of mechanically activated arsenopyrite were investigated. The rate of nonoxidative decomposition of mechanically activated arsenopyrite was increased almost 10 – times when compared with nonoxidative decomposition of a non-activated sample. An empirical linear relationship was found ($r = 0.996$) between the rate constant of decomposition and the ratio of specific surface to transmission of the absorption band of arsenopyrite at $\bar{\nu} = 370\ \mathrm{cm}^{-1}$. This relationship enables us to arrange the reaction $4FeAsS \rightarrow 4FeS + As_4$ among structure-sensitive reactions.

Keywords: arsenopyrite, mechanical activation, thermal decomposition

Introduction

Arsenopyrite is a mineral which does not have any great practical importance if it occurs in the pure form. Provided it occurs as an admixture in the concentrates of non-ferrous metals, the presence of arsenic brings up problems in the course of extraction of these metals as well as problems from the point of view of environmental protection. The importance of this mineral increases if it occurs in association with gold. The extraction of gold usually proceeds in the sequence: flotation → oxidative roasting → cyanizing. The most problematic step is oxidative roasting because the volatile oxides are toxic and improper conditions cause entrainment of gold with flue dust.

The application of mechanical activation which affects the solid state properties by the effect of mechanical forces [1, 2] may be a contribution to the solution of this problem. The mechanical activation makes possible [3–5]

– to raise the retention of arsenic in the solid phase and thus to limit its transition into volatile toxic form,

– to reduce the temperature of oxidative decomposition owing to which the entrainment of gold with flue dust decreases and its metal content in the charge for cyanizing increases.

The mechanical activation reduces the unfavourable effects of roasting but does not eliminate it from the technological scheme. An alternative solution consists in the application of non-traditional methods of arsenic extraction. From the view-point of thermal analysis the method of roasting in inert medium is interesting [6].

The aim of this study has been to investigate the influence of mechanical activation of arsenopyrite on the rate of its decomposition in argon atmosphere and to confront the results obtained with the changes in physico-chemical properties of this mineral.

Experimental methods

The investigations were carried out with arsenopyrite originating from Pezinok (Slovakia) with the following composition: 21.20% Fe, 25.12% As, 10.84% S, 2.55% SiO_2, 0.05% Cu, 3.43% Ca, 0.77 insoluble rest. Beside the basic mineral, the presence of small amounts of quartz, ankerite and calcite was detected by X-ray diffraction analysis.

The mechanical activation of samples was performed in a planetary mill Pulverisette 4 (Fritsch, FRG) under the following conditions: volume of grinding chamber 350 ml, weighed amount of sample 25 g (grain size 0.1–0.5 mm), grinding ball charge: agate balls (15 pieces Ø 10 mm + 11 pieces Ø 20 mm), grinding medium: 25 ml of CH_3OH, relative acceleration of the mill $b/g = 10.29$, grinding time $t_{PM} = 5–120$ min.

The products of grinding were characterized by specific surface area measurements as well as by X-ray diffraction analysis and infrared spectroscopy. The specific surface area was determined from low-temperature nitrogen adsorption with an instrument Areometer (Ströhlein, FRG). The X-ray diffraction phase analysis was carried out with an instrument DRON 2.0 (Techsnabexport, USR) under the following cinditions: Cu-anode, graphite monochromator, $U = 36$ kV, $I = 20$ mA, time constant 0.5 s, sensitivity 10^3 impulses s^{-1}, shift in counting tube 0.067 grad s^{-1}, chart drive 6.66×10^{-4} ms^{-1}. The infrared spectra were taken using the potassium bromide pellet technique (dilution 1:400). The transmission T of the absorption band of FeAsS [7] corresponding to the stretching vibration of the Fe–As bonds was evaluated at $\bar{\nu} = 370$ cm^{-1}.

The thermal decomposition of arsenopyrite was investigated in a dynamic reactor in a static bed of the solid phase under the following conditions: weighed amount of sample 100 mg, flow rate of argon $3.3\cdot10^4$ $dm^3\cdot s^{-1}$, temperature 693–1023 K, reaction time 0–1200 s. The experimental results were processed using the Ginstling-Brounstein equation [8]

$$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=kt \qquad (1)$$

where α, t and k are the conversion degree, reaction time and apparent rate constant, respectively.

The temperature dependence of the decomposition of arsenopyrite was described by the Arrhénius equation from which the experimental activation energy of decomposition was calculated.

Results and discussion

The thermal decomposition of arsenopyrite in inert medium obeys the following equation

$$4\mathrm{FeAsS}\rightarrow 4\mathrm{FeS}+\mathrm{As}_4 \qquad (2)$$

In agreement with this equation we disclosed the formation of pyrrhotine by X-ray phase analysis and identified a black ring corresponding to arsenic in elemental form on the walls of the quartz reactor outside the reaction zone. A detailed microscopic investigation of the phase transformations occurring in the course of arsenopyrite decomposition in inert atmosphere was performed by Cejchan [9].

According to this author, the arising pyrrhotine advances from the surface into the bulk of arsenopyrite, fills the cracks in its grains and following this a transformation of individual particles of the mineral into spongy aggregates of pyrrhotine can be observed. We assumed that the properties of the solid-phase product limit the progress of reaction (2) and determine its mechanism in the region controlled by diffusion. The remainders of arsenopyrite disappear at 973 K and the pyrrhotine sponge entirely fills the particles.

In Fig. 1 the values of the rate constant of decomposition k are plotted against the grinding time t_{PM} (temperature T = 825 K). The mechanical activation accelerates the decomposition almost by one order of magnitude ($k = 0.15\times10^{-6}\ \mathrm{s}^{-1}$ and $1.41\times10^{-6}\ \mathrm{s}^{-1}$). The values of the experimental activation energy E of the decomposition of FeAsS calculated from the Arrhenius equation for the temperature interval T = 639–1023 K are represented as a function of grinding time in Fig. 2. The values are typical of heterogeneous processes the rate determining step of which is diffusion across the layer of a solid product [10]. Owing to the labilization of the bonds of mechanically acti-

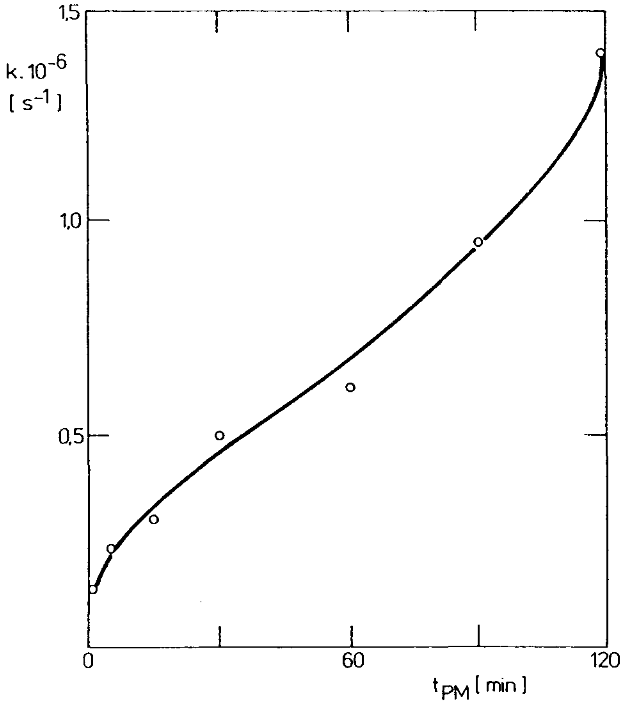

Fig. 1 Rate constant k of arsenopyrite decomposition as a function of the time of mechanical activation t_{PM}. Reaction temperature 825 K

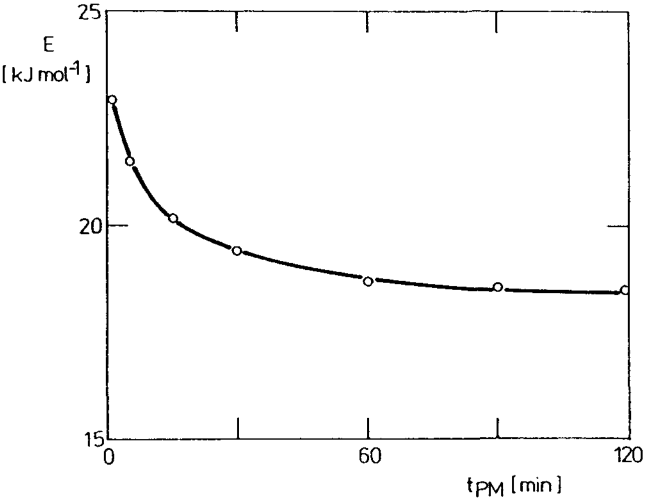

Fig. 2 Variation of specific surface S_A (curve 1) and transmittance T (curve 2) with the time of mechanical activation t_{PM}

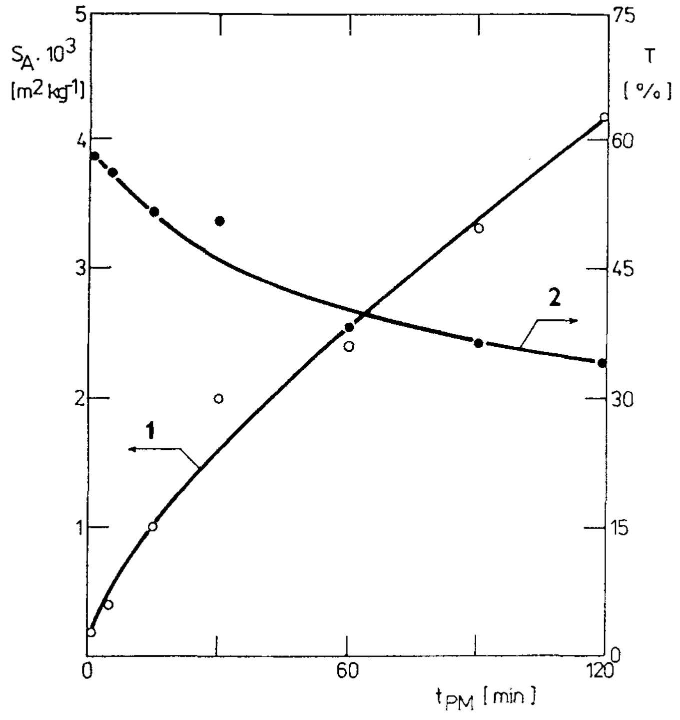

Fig. 3 Experimental activation energy E of arsenopyrite decomposition as a function of the time of mechanical activation t_{PM}. Reaction temperature 639-1023 K

vated samples, the value E decreases with increasing grinding time. At the same time, we can observe a decrease in the response of E to grinding time which may be the consequence of an increased tendency of ground particles to recombination.

The process of mechanical activation of arsenopyrite is accompanied by changes in its solid state properties. In Fig. 3 the values of the specific surface area S_A (curve 1) as well as of the transmittance T (curve 2) are represented as a function of the time of mechanical activation. While the quantity S_A is a measure of formation of new surface of the dispersed particles, the quantity T obtained by evaluating the infrared spectra can be used as a measure of structure disorder of the mineral. In literature the possibility of using infrared spectroscopy for characterizing the degree of crystallinity of kaolin, quartz and orthoclase [11] has been discussed and the relationship between grinding time and transmittance of pyrite at $\bar{\nu}$ = 340 and 411 cm^{-1} was presented [12]. The course of the change in S_A and T in Fig. 3 indicates an increase in surface and structure disorder of arsenopyrite due to mechanical activation.

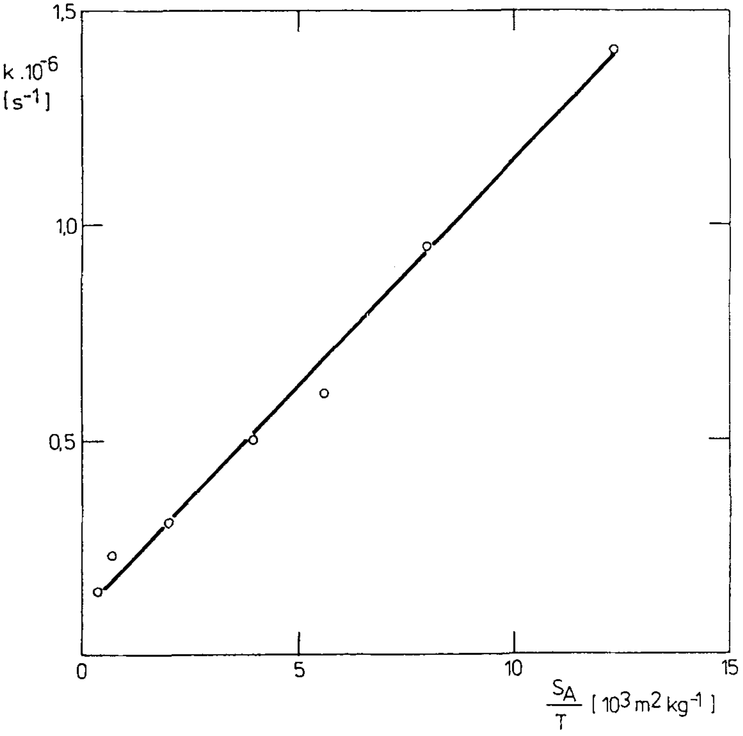

Fig. 4 Variation of rate constant k of arsenopyrite decomposition with the ratio S_A/T. Reaction temperature 825 K

The elucidation of the relationship between structure and reactivity is a dominant problem in solid-state chemistry. The relationship between surface-structure changes and reactivity of mechanically activated samples of arsenopyrite is represented in Fig. 4. This relationship is linear in the investigated region and can be described, with a high degree of correlation (r = 0.996), by the following empirical equation

$$k = (0.111 + 0.103\, S_A/T)\cdot 10^{-6} \qquad (3)$$

In connection with our preceding studies in which we found structure-sensitivity of the reactions of chalcopyrite and sphalerite of the solid-liquid [13] or solid-gas [14] type we can also document on the basis of equation (3) the structure-sensitivity of reaction (2) which is a case of heterogeneous reactions of the type solid$_1$ → solid$_2$ +gas.

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Zusammenfassung — Es wurden Änderungen der spezifischen Oberfläche und struktureller Fehlordnungen von mechanisch aktiviertem Arsenopyrit untersucht. Verglichen mit der nichtoxidativen Zersetzung von nicht aktivierten Proben stieg die Geschwindigkeit der nichtoxidativen Zersetzung von mechanisch aktiviertem Arsenopyrit auf fast das 10-fache an. Zwischen Geschwindigkeitskonstante der Zersetzung und des Quotienten aus spezifischer Oberfläche und Transmission der Absorptionsbande von Arsenopyrit bei $\bar{v}=370$ cm^{-1} wurde eine empirische lineare Beziehung ($r=0.996$) gefunden. Diese Beziehung ermöglicht es, die Reaktion $4FeAsS \rightarrow 4FeS + As_4$ den strukturempfindlichen Reaktionen zuzuordnen.