

Reaction Capacity of Mechanically Activated Tinstone

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Abstract

An effect of mechanical activation on reaction capacity of tinstone under its dispersion with the minerals with different hardness and in the presence of reducing agents was investigated. Dependence of degree of SnO₂ dilution in HCl on the hardness of the added under grinding mineral and on redox capacity of used reagents was fixed. It was determined that an activation barrier decreases with increasing reaction capacity.

INTRODUCTION

Activation by grinding of minerals, so called mechanochemical activation, gives large possibilities to intensification of chemico-concentration processes. Grinding in mills with raised level of mechanical effects causes changes in crystalline structure of minerals. It results in an increase in their chemical activity.

Possibility of increase in the reaction capacity of tinstone was studied for improving the processes of extracting tin and other valuable constituents from it. It is known that tinstone is extremely inert with respect to aggressive media. The problems of increasing its chemical activity are interesting in connection with considerable concentration in mineral structure of such valuable components as Nb, Ta and others, whose extracting on the base of hydrometallurgical method is one of the promising directions.

INVESTIGATION TECHNIC

Monomineral fraction of tinstone from the Deputatsk deposit (Yakutia) was used for test-

ing. Activation by grinding were carried out in a centrifugal mill M-3 in air and water media in steel drums using steel pellets during 5, 15, 20 and 30 min. Thermostats with a mixer and reverse refrigerator were used for studying dissolving kinetics of tinstone. Calorimetric studies were carried out on highly sensitive differential microcalorimeter MKDP-2. To prevent iron effect, the activation of mineral was carried out in a drum with agate fettling. Reaction capacity of SnO₂ was estimated by degree of mineral dilution in concentrated HCL. When studying the reaction capacity of tinstone, the main attention was paid to the effect of additions of some metals with reducing action (Fe, Al) and oxidizers, in particular, KMnO₄ on mechanochemical transformation of mineral. Besides, an abrasive effect of the minerals with different hardness on amorphisation of a structure and on chemical activity in the process of their joint grinding with tinstone was studied. Activation products were studied by X-ray structural analysis (a diffractometer DRON-3, CuK_α radiation).

RESULTS AND DISCUSSION

Physical methods of studying when estimating a degree of mechanical activation

A specific surface continuously increases under tinstone dispersion with water, however structural changes are insignificant and a degree of Sn extracting into muriatic solution does not exceed 25 %. A specific surface of SnO₂ pounded by the dry method; due to aggregate formation even decreases with duration of grinding, *i. e.*, in 5 min it makes up 10.1 m²/g, in 30 min – 6.8 m²/g. Under the following desaggregation of these samples in water it increases by a factor of 2–3, yet it does not reach a value characteristic to water grinding. A degree of tinstone dilution activated in air continuously increases with raising activation time achieving 98.5 % in 30 min.

According to the data of X-ray structural analysis, structural parameters (crystallite sizes, microdistortion value), increase in cymate with the growth of reaction capacity of a mineral [3]. Under grinding in air, the greatest conformity is observed between a degree of dilution and a microdistortion value. Under water grinding, on the background of significant increase in a specific surface the basic constituent of the changes in thin crystalline structure is a dispersion of crystallites, but this does not affect so much the change of reaction capacity as the increasing number of microdistortions.

Experiments carried out in mills with different level of mechanic effect also confirm a thesis that microdistortions and not the crystallite sizes should be considered as a determinant factor of increase in reaction capacity.

As it is known, one cannot explain all physicochemical transformations under mechanical activation by the fact of changes in structural parameters. In the process of mechanical impacts active excited states appear, oxidation and reduction take place in solid phase in the sights with bond rupture and deformation of mineral structure [4].

The comparison of dilution value of tinstone activated with different additions in the M-3 mill in air during 5 and 20 min under the same other conditions is shown in Fig. 1. One

can see that the greatest dilution value of SnO₂ (99.8 %) is marked with using metallic iron as an addition as early as in 5 minutes of activation. Considerable amount of Fe is entered under tinstone dispersion due to abrasion of a mill drum and steel balls material. Therefore, its reduction effect becomes apparent in such or another degree in each experiment carried out. With the addition of Al a tinstone dilution value became by 16 % lower than with the use of Fe [5]. In this case, due to low hardness and abrasiveness of Al with the obtaining definite size by particles, the process of grinding slows down in comparison with grinding in the presence of Fe; cementation of material takes place and during the following mechanical treatment dissolving of SnO₂ changes to a less extent. At the same time, according to the X-ray analysis, in the samples of tinstone activated in a mill with Al, solid phase reduction of tin is registered. Besides the SnO₂ reflections, the main reflections of Sn β-form are fixed in diffraction pattern 3 (Fig. 2) practically with the same intensity ($d_{\alpha/n} = 2.91, 2.79, 2.06, 2.02$). A phase of element Sn is not observed in X-ray diffraction patterns under abrasion of a mixture of SnO₂ with Fe, but such a tin forms as SnO and Sn²⁺ were recorded with the help of Mössbauer spectroscopy in the work [6], which is the evidence of solid phase reduction of SnO₂.

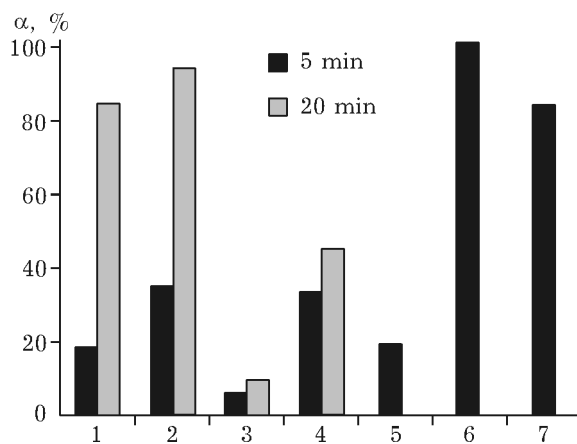


Fig. 1. Diagram of the dilution of tinstone pounded with different additions: 1 – quartz, 2 – topaz, 3 – tiff, 4 – graphite, 5 – KMnO₄, 6 – Fe, 7 – Al.

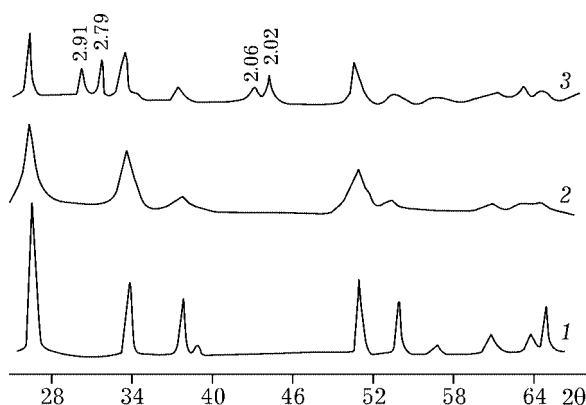


Fig. 2. Diffraction pattern of initial tinstone sample (1), mechanically activated during 5 min with Fe (2) and Al (3).

Under activating of tin oxide (IV) without participation of reducing agents, centers of Sn^{3+} type can also become stabilized, the evidence of which are paramagnetic centers of O_2^- type, formed under chemisorption of oxygen [7]. Besides that, the authors of this work fixed a decrease in solidity of Sn-O bond in mechanically activated SnO_2 , with different level of formation enthalpy, caused by ion-radical formation. It changes from 420 kJ/mol for the initial sample to 340 kJ/mol for the activated in a mill one.

Reduction of tin in the solid phase is one of the determinant factors of SnO_2 dilution in acids. We established that extraction of tin into solution to a great extent goes during the Sn reduction from tinstone by active hydrogen, evolved under the interaction of acid with metals (Fe, Al, Zn, etc.) which are formed as a result of rubbing with the use of metal balls and reducers or present as additions for intensification mineral dilution. At the same time, oxidizing processes, which take place under dispersion of SnO_2 with KMnO_4 considerably, decrease a mineral dissolving.

An analysis of tin dilution value with the use of different minerals as regards additions allows ascertaining its dependence on the solidity of added compound. The greatest effect to dilution of SnO_2 is observed under the joint grinding of tin with topaz and quartz the solidity of which according to Mohs scale is 8 and 7, respectively. With temperature decrease of entered in a drum mineral the dissolving of SnO_2 also decreases, structural transforma-

tions to a great extent determining a dilution value of SnO_2 activated in the presences of minerals. Thus, for example, a reflex breadth value (110) of tinstone under its grinding with graphite made up 3.8 mm, with quartz – 7.8 mm, SnO_2 dilution value changing approximately in the same proportion – from 44.0 to 87.3 %. On the other hand, considerable effect to structural changes and dilution value of tinstone are caused by minerals joint grinding with which activates oxidative reactions. So, despite the higher in comparison with graphite solidity of tiff (according to Mohs hardness scale 1 and 3, respectively), not more than 8 % of Sn enters HCl solution from the activated during 20 min SnO_2 with CaCO_3 , with the use of graphite under the same conditions – up to 44 % (see Fig. 1).

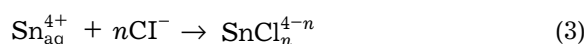
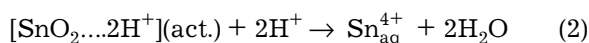
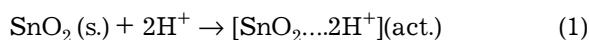
So, a disordering and amorphisation of tin structure take place as a result of mechanical activation, a use of reducing agents in the process of mechanical treatment causes solid-phase reactions, that in whole helps increasing chemical activity of tinstone. Study of the effect of minerals with different solidity, hence, abrasiveness of material allowed to come to conclusion that with decrease in solidity of added compound, structural changes in mineral come down and dissolvable value of SnO_2 decreases.

DILUTION KINETICS OF MECHANICALLY ACTIVATED TINSTONE

Kinetics of mechanically activated samples in HCl solutions was investigated for estimating chemical activity of tinstone. Maximum dilution degree α of grinded in agate drum sample in HCl was 11.3 %. According to diffraction data, tinstone was characterized by some decrease in intensity of reverberation of reflections and by insignificant change in their semi-width.

In preliminary experiments an independence of dilution on the conditions of mixing was fixed for determining a limitative stage of reaction, that is along with high-obtained values of activation energy characterizes the reaction regime as a kinetic one. The reaction order calculated by tangent of angle of a straight

line and set in the coordinates $\lg c - \lg \tau$ (τ is the time required for obtaining the same dilution degree, c is the concentration of solution) is equal to 2. Assumed mechanism of the process of SnO_2 dilution in HCl consists in adsorption of two ions H^+ other each conventional particle SnO_2 with the formation of activated complex:



Activation energy was determined upon kinetic curves of dependence of dilution rate on temperature within the interval of 72 to 95 °C as the ratio of dilution rates under different temperatures and the same depth of SnO_2 transformation (Fig. 3) [8]. Under the chosen conditions this reaction is irreversible, that is why it is possible to change the rates ratio to more exactly determined ratio of time intervals required for obtaining the same dilution degree. Activation energy of SnO_2 dilution in HCl was calculated over different levels of sample transformation within the region $\alpha = 3.5$ –5.5 % as a tangent of straight line incline in coordinates $\lg \tau - 1/T$. The example of graphic determination of apparent energy (E_{app}) under three different dilution degrees is shown in Fig. 4. One can see that with increasing α the angle of incline of the straights noticeably increases; hence, the activation energy goes up. With α increasing from 4.1 up to 5.5 % E_{app} grows from 76 to 98 kJ/mol.

Extrapolation of the data obtained to the initial moment of tinstone dilution leads to considerably lower E_{app} values than obtained ones, since by the moment of their determination chemically active part was already in solution. On the whole, one can suppose that as less and less active layer of mineral particles enters the reaction, energy of activation barrier increases. From this it follows that grinding of hardly soluble minerals of tinstone type causes change in chemical activity of a matter in different degree for various crystal layers.

Activation energy for initial sample was not determined because of extremely low dilution of not activated tinstone ($\alpha = 0.001$ %). Based

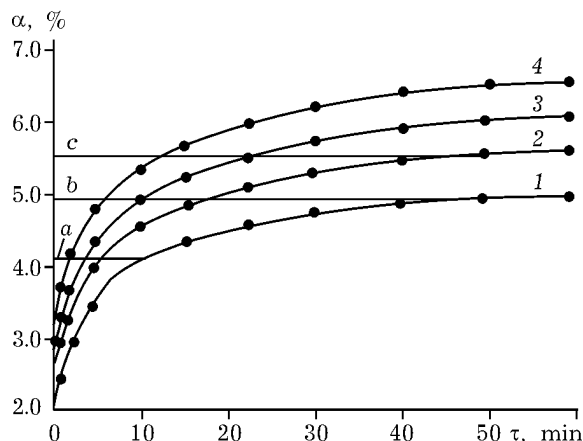


Fig. 3. Kinetic curves of dilution of mechanically activated SnO_2 under different temperatures, °C: 72 (1), 82 (2), 88 (3), 95 (4). E_{app} , kJ/mol: 76 (a), 90 (b), 98 (c).

on the regular increase in E_{app} with decrease in reaction capacity of mineral, it can be proposed that it is characterized by yet more high activation energy in comparison with fixed in experiment one.

Based on calorimetric changes, a proportional dependence between the reaction capacity of a mineral and the heat of its dilution in HCl was revealed for activated by grinding tinstone, all the data obtained are considerably (by 25–50 kJ/mol) differ from calcula-

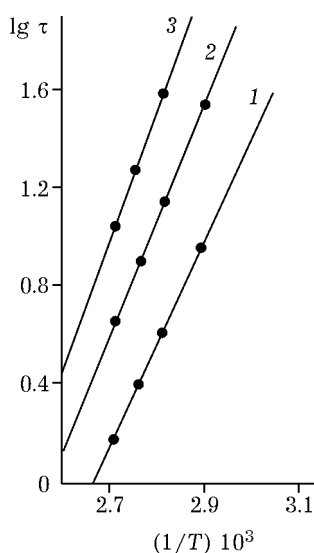


Fig. 4. Dependence of $\lg \tau$ on $1/T$ under different dilution degrees of SnO_2 (according to the data of Fig. 3), %: 4.1 (1), 4.8 (2), 5.5 (3).

tion enthalpy values of the reaction of crystalline SnO₂ dilution.

CONCLUSION

Dispersion of tinstone in highly strained mills causes the profound structural-chemical transformation and leads to change in energy state which appears in decrease in the activation energy and correspondingly in increase in mineral dilution in acids. A procedure of mechanical activation also allows carrying out solid-phase reactions, including reducing effect, promoted an additional extraction of tin into acid solutions. Besides, with its help one can improve hydrometallurgical processing for the purpose of complex extraction along with the basic compound (tin) concomitant expensive elements.

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