INCREASE IN INTERNAL ENERGY AND MECHANISM OF QUARTZ GRINDING

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A method was worked out for determining the increased energy content supplied to quartz by grinding, by measuring the exothermic effect in DTA. Measurements performed after certain selected times of grinding show that liberation of energy starts within the temperature interval of 110°C ± 10 °C and exhibits several peaks. The first peak, arising in particular with quartz after short times of grinding, appears at 325 °C ± 15 °C and tends to shift towards lower temperature within this range with increasing time of grinding. The second peak lies at 420 °C ± 20 °C, while the third one at 540 °C ± 10 °C, being overlapped by the second one when the time of grinding increases. The paper also shows the effect of surface active substances on the growth of internal energy of quartz in the course of grinding, and brings evidence on an increase in internal energy due to the grinding of 'amorphous' substances such as quartz glass. The results were employed in the formulation of certain conclusions with respect to the mechanism of grinding.

INTRODUCTION

The effect of grinding on the structure of quartz has been dealt with by numerous authors for a number of years [1]. There are two basic concepts of the way in which grinding affects the structure of quartz. According to Adamtschik [2] free radicals arise on the surface of split planes so that on interruption of the Si-—O bond the oxygen retains an electron, thus acquiring a negative charge, and a positive one arises on silicon. These free radicals, bound to quartz surface by further two or three bonds, however, may also arise in cracks inside the quartz crystal. Brittle fracture of crystals is therefore assumed to take place.

According to Chodakov [3], [4], [8] plastic deformations on the surface of crystals bring about amorphization of a certain layer, the thickness of which (20 Å to 0.16 μm) depends not only on the conditions and time of grinding [3], [4], [5], [6], [7] but also on the method employed in the determination of particle size [4] where particle size calculations based on specific surface area provide excessively large thicknesses of the amorphized layer. However, these questions have already been explained earlier [9], [10], [11] by showing that adsorption methods do not determine the total particle surface area S_c but only the free one S_v and a certain part of the surface S_n, the size of which increases with decreasing particle size and polydispersity of the system, becomes inavailable for the adsorption particle molecules. This is why the particle sizes determined in this way are always larger than the actual ones, and a certain surface effect thus may appear as one taking place inside the particles. For this reason a great deal of attention has been paid to the problems

of correctness, applicability interval, interpretation and mutual relations between the results obtained by certain methods frequently employed for characterizing the particle size of ground substances [10], [11], [12] since without this study it would be impossible to distinguish the effect of grinding on the change in particke size, on the changes in the structure of solids, and to evaluate the significance of particle agglomeration.

According to the first concept the formation of free radicals in split areas would bring about an increase in the internal energy of quartz which would be released in the course of heating up so that the entire process would appear as an irreversible one in DTA. This was actually shown to be the fact [13], [14], [15]. The exothermic effect was found to begin in the 105 °C to 120 °C temperature range. The first exothermic peak arising with short times of grinding appears at 325 °C ±15 °C, and tends to shift towards lower temperatures with the time of grinding. The second peak lies at 420 °C ±10 °C and the third one at 540 °C ±15 °C. With increasing time of grinding the entire effect is shifted towards higher temperatures, being concluded at about 650 °C under the given grinding and DTA conditions [14], [15].

In view of the three peaks arising on the effect plane [14], [15] it is hardly possible to consider formation of a crystalline structure in the amorphized substance. The process involved is obviously structural rearrangement in various crystallographical planes, where to each distance between crystallographic planes there corresponds a certain vibration energy value and thus also a certain amplitude pertaining to a certain temperature.

It is the opinion of many authors that grinding thus affects the rate of chemical reactions, being even the necessary precondition for some of them. The respective relations and processes are dealt with by tribochemistry [16].

THE METHOD FOR DETERMINING THE INCREMENT IN THE INTERNAL ENERGY OF QUARTZ

The increase in internal energy of quartz in terms of the time of grinding was determined by means of the DTA apparatus manufactured by Laboratorní přístroje, National Corporation, and adapted by the author in order to increase accuracy and sensitivity [17].

The experimens employed glassmaking quartz sand *T*-optika with small amounts of additives; the material was ground for periods of 30, 60, 120 and 240 minutes in vibration mill M10 of Soviet manufacture. The amplitude was 2.25 mm, frequency 2780 r. p. m., the degree of mill charging was 0.8, the quartz sand charge was 3 kgs and that of dia. 9 and dia. 15 grinding steel balls was 39 kgs. The nominal input of the mill was 4.5 kW, the actual one 1.8 kW.

The DTA record of ground quartz is affected by the following factors:

1. The course of modification transformation of quartz (reversible)
2. Grain size of the sample [17]
3. Liberation of heat supplied to the solid (quartz) during its grinding by impairing the bonds between the individual $(SiO_4)^{-4}$ tetrahedrons. The process is irreversible.

Since the temperature range in question does not affect the grain size of the sample (by sintering), the thermal conductivity of the samples will be identical in repeated measurements. Liberation of the increment of quartz internal

energy due to grinding will usually take place during the first heating. However, in some cases the heating has to be repeated, in particular with samples ground for longer periods of time and those whose heating has been concluded at lower temperatures. This temperature is given by the time as well as by the conditions of grinding. Quartz can be determined quantitatively only after eliminating the defects in the structure of the quartz-containing substance. This last determination which no longer shows any liberation of heat, can be regarded as a standard line for evaluating the liberated energy (ΔQ) which is proportional to the peak surface area (ΔP) between this standard line and the curve given by the record of the first determination:

$$\Delta Q = k\Delta P \tag{1}$$

where k is a proportionality constant representing the amount of heat corresponding to peak unit area (cal/rel.cm²) which depends on the type and adjustment of the apparatus and the experimental conditions. Its value is est abshed by calibration using a know sample.

In the case when the standard line required the measurement to be repeated n-times.

$$\Delta Q = \sum_{i}^{n} Q_i = k \sum_{i}^{n} \mathrm{V}P_i \tag{2}$$

However, for the sake of simplicity it is better not to repeat the measurement but to raise the final temperature during the first heating.

Such a simple calculation would require a constant rate of heating. Since the peak size at a constant value of liberated heat depends on the rate of heating at this temperature, the calculation is more complex. As, however, every regulation aimed at a constant rate of temperature increase requires to increase heating current with temperature and the current causes induction in the measuring system and complicates both the apparatus and the evaluation, the measurement was carried out with the use of constant heating current. This was ensured by a current stabilizer [17]. The measurement was thus effected at a variable (decreasing) rate of temperature increase; in this way there takes place a continuous but non-uniform change in the value of the constant in relation (1) with heating temperature. For this reason the peak area was divided into narrow temperature intervals, and the value of reduction coefficient k- was determined for recalculating the area at the given rate of heating (ΔP_i) to the rate selected as standard (P_{19}). In the present case this was a rate of heating of 19 °C/min at which the relationship was established between the liberated (consumed) energy and the peak area. Use was made of pure cristobalite for the following reasons: it has a relatively narrow transformation temperature interval, a suitably large transformation heat, and finally the transformation takes place at a satisfactorily low temperature to permit to carry out measurements within a wide range of heating rates in the given apparatus. At has already been mentioned, the reduction coefficient value is given by the relation

$$k_{r_i} = \frac{\Delta P_{19}}{\Delta P_i} \tag{3}$$

The relationship between the peak area of pure cristobalite and the rate of

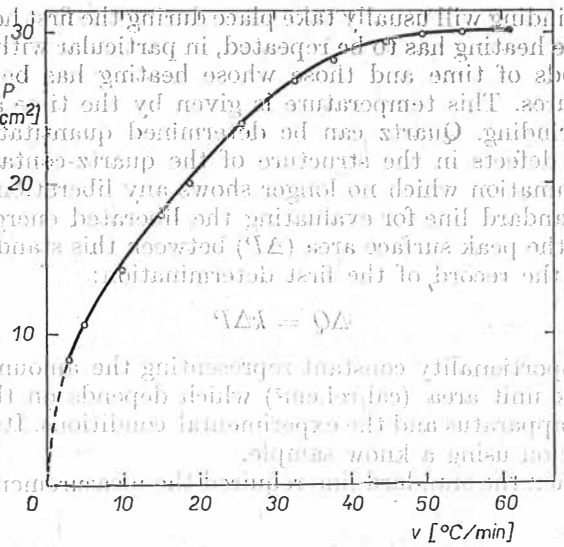

Fig. 1. Peak area of pure cristobalite vs. rate of temperature increase in DTA.

temperature rise in DTA is illustrated in Fig. 1. The diagram shows an almost linear relation of the peak area and the temperature rise rate within a wide range of heating rates, which decreases rapidly to zero below 5 °C/min and approaches a certain limiting peak area when the heating rate is increased. To this also corresponds the course of the reduction coefficient value in terms of DTA temperature increase rate shown in Fig. 2. Below 5 °C/min its value increases rapidly, above this rate it changes from 2 to 0.66 at heating rates

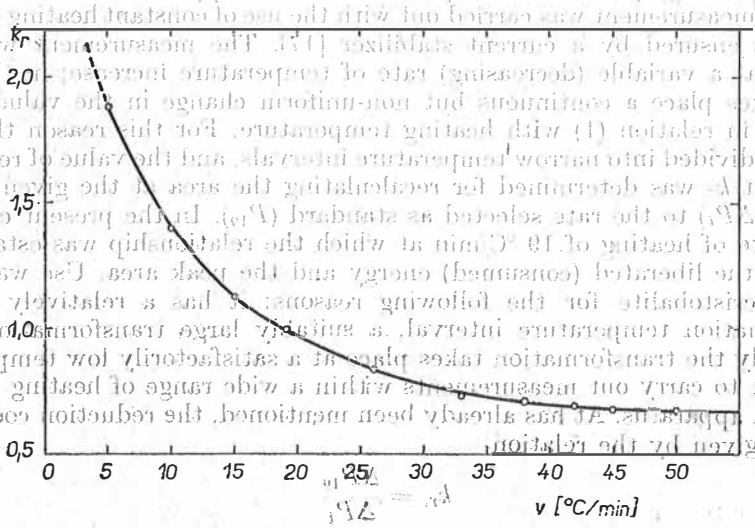

Fig. 2. Reduction coefficient value vs. rate of temperature increase in DTA.

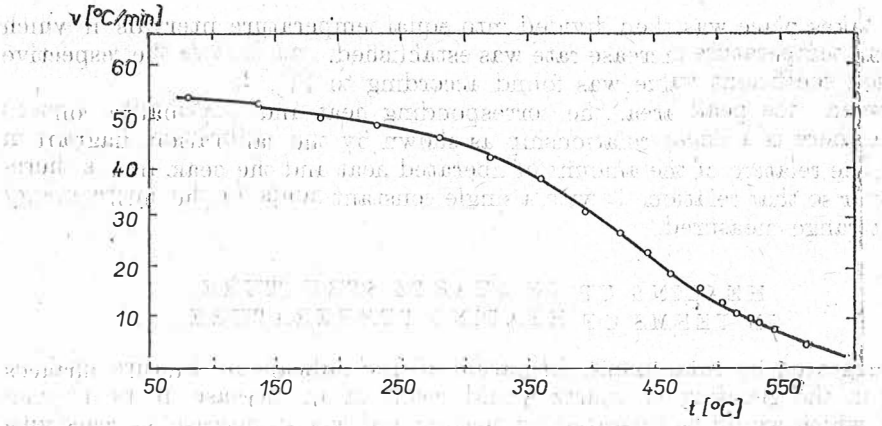

Fig. 3. Rate of temperature increase vs. temperature in DTA of quartz.

higher than 45 °C/min (obviously in view of the negligible heat dissipation losses when compared with the heat supplied).

The rate of temperature increase is constant at a certain temperature when the DTA conditions are maintained constant and for this reason the relationship between temperature increase rate and temperature was determined within the interval up to the maximum temperature employed for DTA of quartz (Fig. 3) and the entire interval where liberation of free energy of

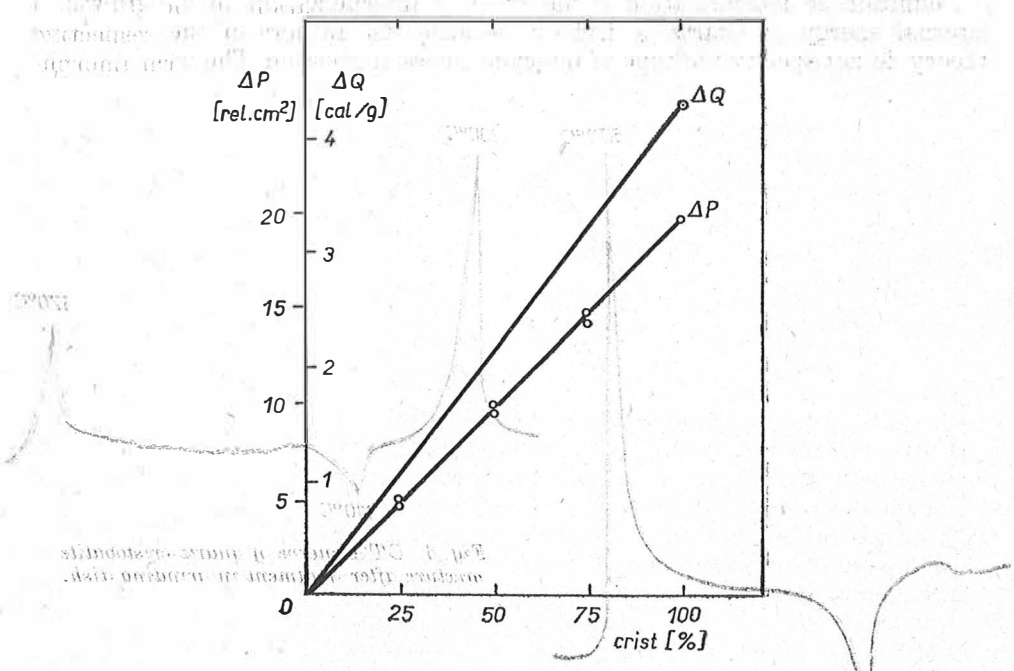

Fig. 4. Calibration diagram. Peak area (ΔP) [rel cm²] and amount of corresponding liberated heat (ΔQ) [cal/g] in DTA vs. cristobalite content.

quartz takes place was then divided into equal temperature intervals in which the mean temperature increase rate was established, and for this the respective reduction coefficient value was found according to Fig. 2.

Between the peak area, the corresponding heat and cristobalite content in DTA there is a linear relationship as shown by the calibration diagram in Fig. 4. The relation of the amount of liberated heat and the peak area is therefore linear so that relation (1) with a single constant holds for the entire energy content range measured.

HEALING UP OF QUARTZ STRUCTURE IN TERMS OF HEATING TEMPERATURE

As suggested by Adamtchik, formation of free radicals on fracture surfaces arising in the grinding of quartz would result in an increase in its internal energy, which would be liberated by heating and would increase its reactivity towards other substances. It was therefore established from what temperature upwards this increased energy is released, what is the temperature dependence of energy liberation, at what temperature the entire process of elimination of free radicals (or release of increased energy) has been practically concluded and how these relations change in terms of the time of grinding.

The questions concerning the conditions for utilizing this increased energy in solid phase reactions, although already discussed by various authors [18], [19], are exceedingly complex owing to the difficult methods involved [11] and will therefore not be dealt with in the present study.

Definition or determination of the effect of amorphization on the growth of internal energy of quartz is difficult because the authors of the respective theory do not specify the type of amorphousness in question. The term amorph-

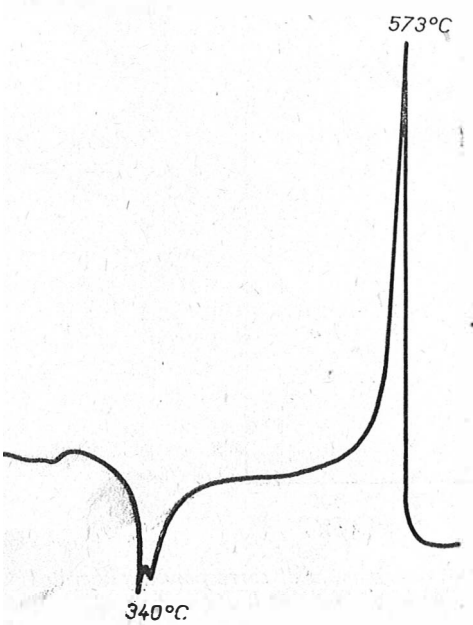

Fig. 5. DTA curve of quartz after treatment in grinding dish.

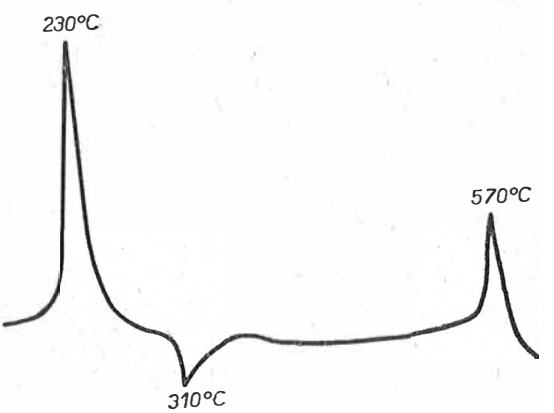

Fig. 6. DTA cuerve of quartz-cristobalite mixture after treatment in grinding dish.

ous substances has so far concerned substances having no crystalline structure. However, different behaviour will be exhibited during grinding by substances composed of individual non-arranged molecules (silica gel heated at low temperature) or mutually non-arranged but almost totally linked $(SiO_4)^{-4}$ tetrahedrons (quartz glass). According to Chodakov's definition amorphization takes place as a result of plastic deformations, so that one might conclude that the amorphous layers has rather the character of silica gel. In that case, however, this would involve formation of a new substance having new properties, the energy supplied would be consumed in creation of this new substance having another conntent of internal energy; however. this energy would not be released by heating, being a characteristic quantity of the new substance.

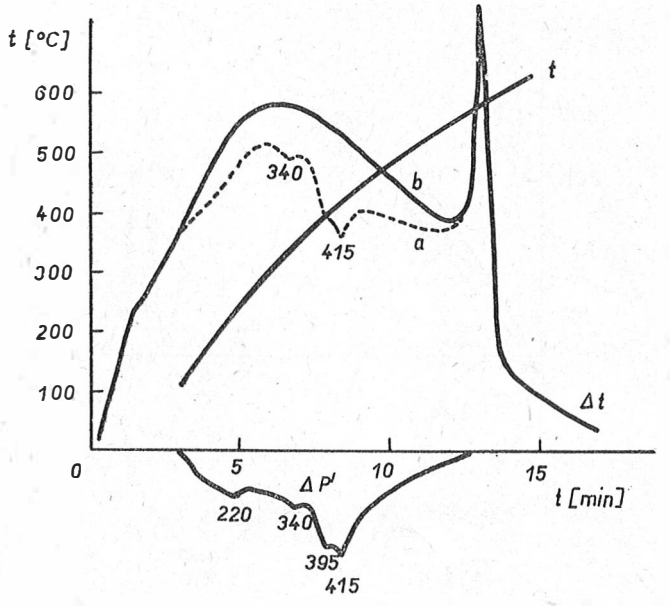

Fig. 7. DTA curve of quartz sand ground for 30 minutes.
Δt: a — first heating, b — second heating of the same sample, t — temperature rise in terms of time.

In DTA of quartz, energy is actually liberated already following standard treatment of the sample in a grinding dish, as shown in Fig. 5, similarly to the case of quartz-cristobalite mixture as shown in Fig. 6. An exothermic peak having its maximum at 310 °C to 340 °C arises on the curves in both cases. DTA of pure cristobalite pretreated in the same way revealed no such release of energy, probably because treatment of very fine-grained cristobalite produced disintegration in intercrystalline planes where Si—O bonds were not interrupted and free radicals were not formed.

The beginning of this exothermic reaction in the grinding of quartz sand takes place independently of the time of grinding, generally at the same temperature of 105 °C to 120 °C. However, the regeneration of structure depends on the degree of structural damage and thus in the time of grinding.

The DTA record of quartz sand ground for 30 minutes, shown in Fig. 7, indicates that structural regeneration begins at 105 °C, passes in principle through two peaks at 340 °C and 415 °C respectively (taking into account only peaks arising on the original DTA curve) and is concluded in front of the peak corresponding to the β to α-quartz transformation at approx. 570 °C. In the diagram, curve *a* represents the first heating and curve *b* the repeated one which simultaneously serves as a base line in DTA after elimination of all reversible changes.

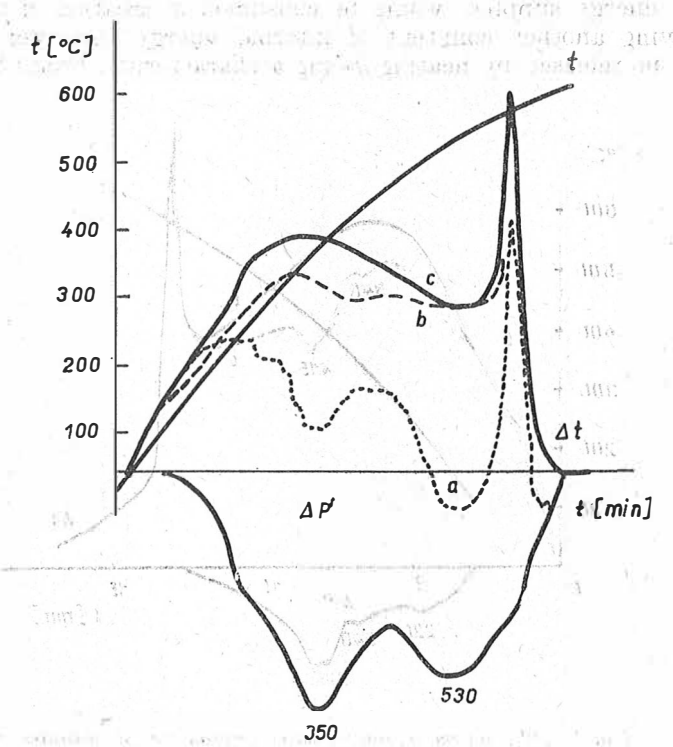

Fig. 8. DTA curve of quartz sand ground for 60 minutes. Δt: a — first heating, b — second heating, c — third heating of the same sample, t — temperature rise in terms of time.

After grinding for 60 minutes (Fig. 8) the exothermic DTA effect grows and a new peak appears at 530 °C, while no peak appears at 415 °C. The final effect temperature was also raised above the quartz transformation point. In view of the fact that the first measurement was concluded at a relatively low temperature, further energy release took place during the repeated measurement *b*. The measurement was repeated for the third time *c*; it had no effect on the position of exothermic peaks, but affected the peak size and the amount of energy released. The total area of the exothermic effect is then equal to the sum of areas obtained in the two measurements. Thus ΔP_a is given by the area between the *a* and *c* curves, and ΔP_b by that between *b* and *c* curves; the total area ΔP is then

$$\Delta P = \Delta P_a + \Delta P_b,$$

of course after adjustment by the reduction coefficients as mentioned above.

The DTA record of quartz sand ground for 120 minutes, shown in Fig. 9 indicates that the peak at 405 °C has grown while those at 310 °C and 550 °C remained unchanged. The DTA record of quartz sand ground for 240 minutes (Fig. 10) shows a further growth of the peak at 430 °C while the peak at 330 °C remained unchanged and that at 530 °C was relatively reduced.

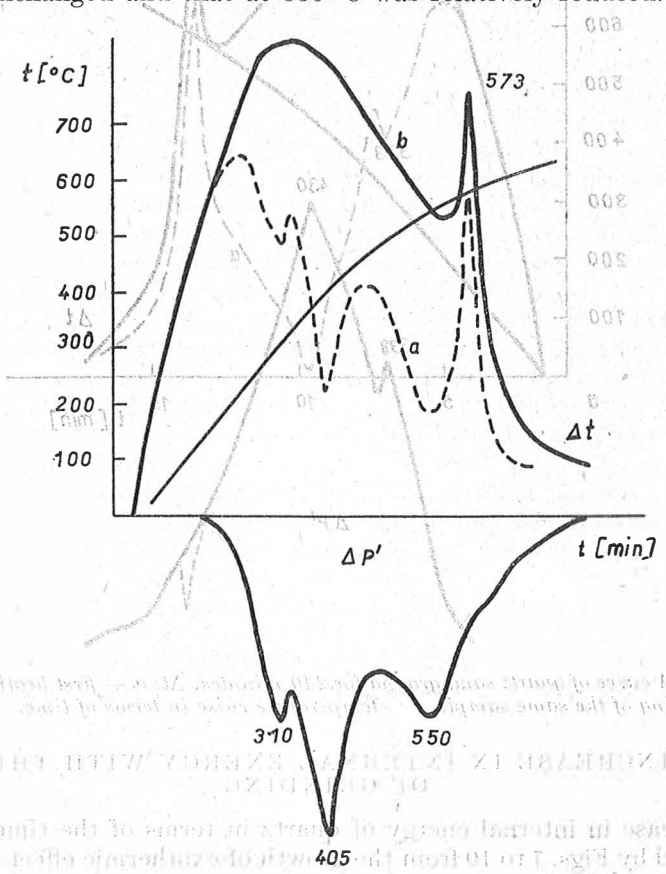

Fig. 9. DTA curve of quartz sand ground for 120 minutes. Δt: a — first heating, b — second heating of the same sample, t — temperature rise in terms of time.

A comparison of DTA records of quartz sand ground for the selected periods indicates that the liberation of energy gebins at 110 °C ± 10 °C with the first peak at 325 ° ± 15°C; with the time of grinding this peak is shifted slightly towards the lower temperature in the interval. The second peak lies at 420 °C ± 10°C and the third at 540 °C ± 10 °C. The entire exothermic effect accompanying the liberation of energy supplied to quartz by grinding, progresses with the time of grinding towards higher temperatures and under the given conditions of DTA the structure is therefore practically regenerated up to 650 °C. The total increment of the internal energy of quartz increases simultaneously with the time of grinding.

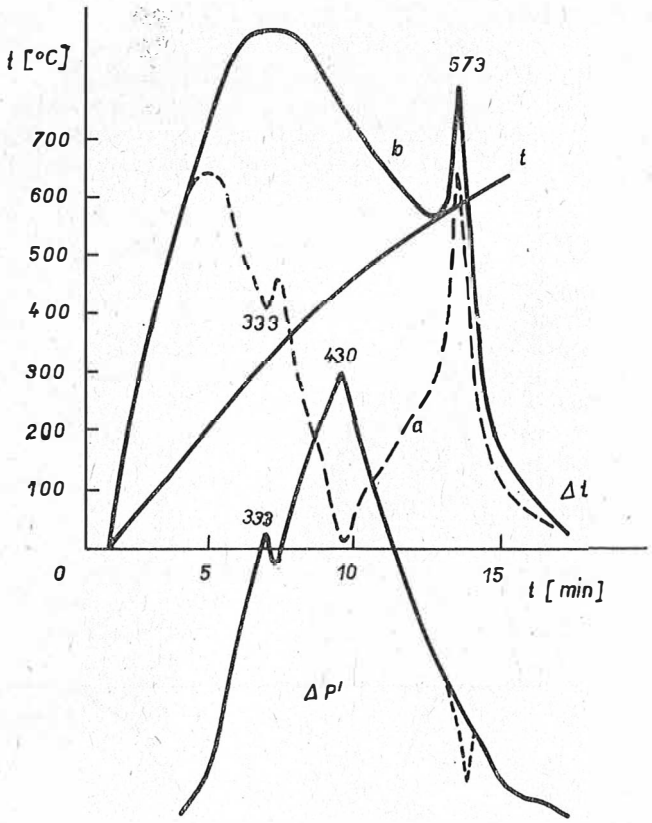

Fig. 10. DTA curve of quartz sand ground for 240 minutes. Δt: a — first heating, b — second heating of the same sample, t — temperature ruise in terms of time.

THE INCREASE IN INTERNAL ENERGY WITH THE TIME OF GRINDING

The increase in internal energy of quartz in terms of the time of grinding is illustrated by Figs. 7 to 10 from the growth of exothermic effect area of DTA. Quantitative evaluation of the amount of energy released during heating is by no means simple under the given conditions, but when complying with the procedure described in Chapter 2 it is practicable. For the purpose of increasing the accuracy of the values obtained the released energy should be measured for each time of grinding on at least two samples and the mean value taken. It is necessary because the energy concentration in the mill volume is not homogeneous so that the grinding proceeds at different rates in various parts of the mill. This is of primary significance for the way of sample taking, reproducibility of results and validity of the respective conclusions. The results are therefore means of at least two effect areas measured and of the corresponding released energy.

The measured values of exothermic effect area growth and the corresponding values of released energy for quartz sand *T*-optika, ground in a vibration mill

under the conditions described above, are plotted in Fig. 11. The increment of the free energy of quartz obviously increases with the time of grinding, but the rate of growth of internal energy decreases with the time of grinding. The change on the internal energy of quartz during grinding has therefore the same character as the change of specific surface area.

This decreasing rate of increase in internal energy of quartz during grinding could be explained by the fact that agglomeration of particles increases with increasing fineness of the solid (quartz) so that a certain part of free radicals found at the point of contact 'reacts' on the renewed Si—O bond and is released in the form of heat already in the mill. A portion of these free radicals which at the given temoperature did not get to the distance of intermolecular forces, remains of course at the surface and is then gradually released in the course of heating. In principle, there are therefore four types of free radicals (ionts) arising during the grinding of a solid (quartz):

1. Free radicals which already get into the distance of intermolecular forces during the grinding process, and are eliminated by being involved in a chemical bond between particles causing agglomeration.

2. Free radicals at the surface which get into the distance of intermolecular forces in the course of heating up, re-establish bonds between the particles and reinforce the strength of links between them. This is the cause of a considerable increase in the strength of products with a compact arrangement of particles, taking place at relatively low temperatures without sintering which has been considered the main cause so far.

3. Free radicals arising in surface cracks or inside a particle, which have either not yet reached the distance of intermolecular forces or even when at this distance, have not yet reacted since even this process has a time dependence or kinetics at the given temperature.

4. Free radicals at particle surface which are far from the reach of intermolecular forces.

As has already been shown earlier, the contact (inavailable) surface of particles (both homogeneous and inhomogeneous) increases with the time of

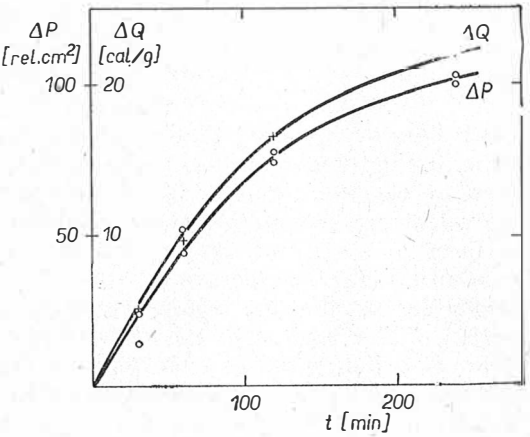

Fig. 11. Increment of internal energy of quartz vs. time of grinding. ΔP ... peak area reduced for rate 19 °C/min, ΔQ ... increment of internal energy of quartz.

grinding, and the increment of free energy of the solid might decrease proportionally.

An addition of surface-active substance, in other words substances capable of settling as soon as possible on freshly arising fracture surfaces, therefore prevents above all the particles from rejoining by re-establishing their mutual bonds, thus preventing their agglomeration and loss of internal energy supplied to the solid in the course of grinding. This effect is well illustrated by Fig. 12 where the increment of free energy of quartz ground without additives—curve *1* — is compared with that obtained with an addition of 0.5 % ethyl alcohol (denatured with methyl alcohol) and 0.5 % concentrated ammonia [22].

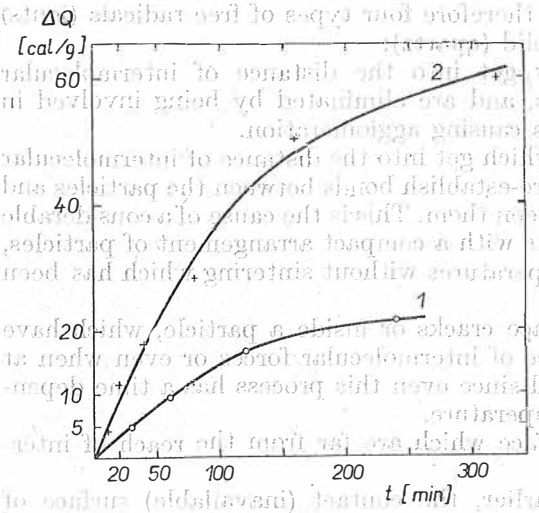

Fig. 12. Increment of internal energy of quartz vs. time and conditions of grinding.
1 ... without additives,
2 ... with additive of metanol-denatured 5 % ethyl alcohol and 0.5 % concentrated ammonia.

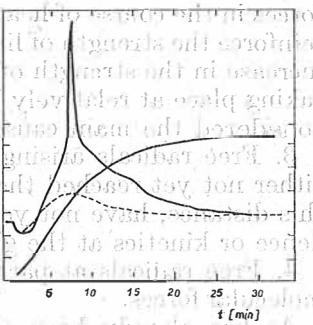

Fig. 13. DTA curve of quartz glass ground for 10 minutes in a vibration mill. t ... temperature, Δt — a ... temperature difference during the first heating, b ... temperature difference during secon heating of the same sample.

That the increase in energy involved that part of quartz energy that had been consumed in the linking (agglomeration) of particles as explained above, has also been proved by the fact that the significance of the individual peak is decreasing in the releasing of energy with the time of grinding, that the total value of free internal energy of quartz increases, and that the entire process is shifted towards higher temperatures.

Another evidence for the fact that the increase in internal energy of the solid is due to the formation of free radicals is that this increment of internal free energy with the time of grinding arises even when grinding an amorphous (non-crystalline) substance like quartz glass [23]. Here, however, the increase appears as a single sharp peak at 340 °C ±15 °C as shown in Fig. 13 for a time of grinding of 10 minutes. Amorphization of an amorphous substance is of course out of question in this case. The internal energy obviously grows due to interruption of chemical (covalent) but strongly polarized Si—O bonds.

Re-establishment of bonds between the particles is likely to proceed in a disorganized manner regardless of whatever type of crystalline form possible with SiO_2. It is therefore possible to admit that a certain amorphization of structure takes place when grinding a crystalline substance (quartz). However, this should be regarded as a secondary process taking place partly in the course of grinding and partly during subsequent heating and concerns solely the surface layer of crystalline particles. The loss in quartz found after grinding is more-or-less a matter of method depending on what property of the solid has been selected as criterial. However, most of the methods used in the determination of a certain phase depend on particle size so that the quantity to be determined must depend on the quantitative effect of a certain material property (DTA on the number of bonds being rearranged or tilted to a new position, infra-red spectroscopy on the number of vibrating atoms capable of absorbing the radiation, X-ray diffraction on the size of crystals). In this way the effect of particle surface area increase must finally appear as a loss in the given phase since the surface molecules of the bond will obviously behave differently than those inside the crystal. A loss in quartz due to grinding does not therefore allow to indicate amorphization as its cause without more detailed study of the correctness and types of data provided by the individual methods.

EVALUATION AND CONCLUSION

It has been found that grinding affects not only the size but also the structure of particles and thus the internal energy of a solid. However, the arising defects are only temporary from the standpoint of heat treatment, and structural regeneration is a function of temperature. The amount of defects, characterized by the surface area of the effect and thus by the amount of heat released by heating, is a function of the time and regime of grinding. Grinding therefore increases the internal energy of a certain crystalline substance. In DTA of crystobalite this effect did not take place obviously because the size of primary cristobalite crystals arising during the transformation was obviously smaller that that of particles employed in DTA, so that treatment of a sample brings about disintegration mostly only at the intercrystalline planes of contact between the individual cristobalite crystals. The finess required for this effect is obviously unattainable when using the grinding dish only.

The measurements have further shown the temperature dependence of structural defectiveness, in other words increased reactivity and the temperature interval within which this is eliminated in quartz. This finding is of obvious significance for solid phase reactions as well as for application of a crystalline substance as catalyst carrier for both organic and inorganic reactions.

The results obtained indicate that the exothermic effect due to release of energy during DTA of quartz may affect (reduce) the amount of quartz determined in the sample since the exothermic effect arising by regeneration of structure (bonds) reduces the exothermic effect due to modification transformation during the first heating. At a high proportion of defective bonds within the transformation interval the error due to this effect may not be negligible when the bond energy is much higher than that involved in the modification transformation.

Since there are three peaks on the effect area, it is hardly possible to con-

sider formation of a crystalline structure in an amorphized substance. It is obviously a case of structural regeneration in various crystallographic planes where to each distance between planes pertains a certain vibration energy value and amplitude for a certain temperature, and thus also a certain peak on the exothermic DTA curve.

However, when considering amorphization as a process involving a damage to the substance structure not connected to the effect of plastic deformations, but in principle comprising interruption of bonds between the atoms of the given substance (in the case of quartz these are the chemico-covalent-polarized Si—O bonds) one can reach the conclusion that the growth of energy required for grinding with increasing particle fineness is based on a growth of internal energy of the substance being ground (quartz); this energy remains partially in the substance even after concluded grinding and partially is released during grinding in the form of heat as a result of re-establishing of bonds. The bonds are re-established to a degree smaller than with the original nonground substance since the fracture plans are not planer and only some of the free radicals are within the distance of intermolecular forces required for re-establishment of bonds at the given temperature. This is finally in agreement with the observations and concepts by Chodakov who suggested that the arising agglomerates are very strong, cannot be split neither by water nor by heating [4], [20] and can be dispersed only when supplying further mechanical energy, as stated in (l) and as observed in the grinding of ZrO_2 where the energy required for preparing samples for electron microscopy was supplied by means of ultrasound [21].

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RŮST VNITŘNÍ ENERGIE A MECHANISMUS MLETÍ KŘEMENE

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Měřením exotermního efektu při DTA je stanoven růst vnitřní energie křemene při mletí v závislosti na době mletí. Tato energie se uvolňuje při zahřívání.

Z porovnání jednotlivých měření je zřejmo, že uvolňování energie začíná v intervalu teplot 110 ± 10°C a probíhá několika vrcholy. První vrchol, projevující se zejména u vzorků s krátkou dobou mletí při teplotě 325 ± 15°C, se s dobou mletí posouvá v uvedeném intervalu k nižší teplotě. Druhý vrchol, jehož význam roste s dobou mletí, leží při teplotě 420 ± 20 °C a třetí leží při teplotě 540 ± 10 °C, je s dobou mletí překrýván vrcholem druhým.

Růst vnitřní energie křemene je způsoben vznikem volných radikálů či iontů, které vznikají v rozštěpných plochách a trhlinách krystalů křemene. To je potvrzeno tím, že hodnota zvýšené vnitřní energie křemene roste v přítomnosti mlecích přísad (povrchově aktivních látek), které brání přiblížení částic na vzdálenost mezimolekulárních sil, a tím i jejich aglomeraci a zániku volných radikálů na povrchu částic. Růst vnitřní energie ovšem svědčí o tom, že hlavní část energie na mletí se spotřebuje na trhání chemických, polarizovaných vazeb Si-O. Názor o růstu vnitřní energie křemene vznikem volných radikálů i mechanismu mletí je potvrzen i tím, že růst energie se projevuje i při mletí amorfní látky, jakou je křemenné sklo, kde však jednotlivé tetraedry SiO_4 nejsou pravidelně uspořádány, avšak jsou vzájemně pospojovány. Zde se však objevuje pro všechny doby mletí v podstatě jen jediný vrchol při teplotě 340 ± 15°C. Počátek i konec děje je podobný jako u křemene.

Dále je uvedena metodika pro stanovení růstu vnitřní energie tuhých látek při mletí.

Obr. 1. Závislost plochy piku čistého cristobalitu na rychlosti stoupání teploty při DTA.
Obr. 2. Závislost hodnoty redukčního koeficientu na rychlosti stoupání teploty při DTA.
Obr. 3. Závislost rychlosti stoupání teploty na teplotě při DTA křemene.
Obr. 4. Kalibrační graf. Závislost plochy piku (ΔP) [rel cm²] a množství odpovídajícího vybaveného tepla (ΔQ) [cal/g] při DTA na obsahu cristobalitu.
Obr. 5. Křivka DTA křemene po úpravě v třecí misce.
Obr. 6. Křivka DTA směsi křemene a cristobalitu po úpravě v třecí misce.
Obr. 7. DTA křemenného písku mletého 30 minut. Δt: a — prvý ohřev, b — druhý ohřev téhož vzorku, t — růst teploty v závislosti na čase.
Obr. 8. DTA křemenného písku mletého 60 minut. Δt: a — prvý ohřev, b — druhý ohřev, c — třetí ohřev téhož vzorku, t — růst teploty s časem.
Obr. 9. DTA křemenného písku mletého 120 minut. Δt: a — prvý ohřev, b — druhý ohřev téhož vzorku, t — růst teploty v závislosti na čase.
Obr. 10. DTA křemenného písku mletého 240 minut. Δt: a — prvý ohřev, b — druhý ohřev téhož vzorku, t — růst teploty v závislosti na čase.
Obr. 11. Závislost přírůstku vnitřní energie křemene na době mletí. ΔP... plocha piku redukovaná na rychlost 19 °C/min, ΔQ... přírůstek vnitřní energie křemene.
Obr. 12. Závislost přírůstku volné energie křemene na době a podmínkách mletí. 1 ... bez přísad, 2 ... s přísadou 0,5 % etylalkoholu denaturovaného metylalkoholem a 0,5 % konc. amoniaku.
Obr. 13. DTA křemenného skla mletého 10 minut ve vibračním mlýně. t — teplota, $\Delta t'$: a... diference teploty při prvním, b ... při druhém ohřevu téhož vzorku.

J. Růžek:

РОСТ ВНУТРЕННЕЙ ЭНЕРГИИ И МЕХАНИЗМ ИЗМЕЛЬЧЕНИЯ КВАРЦА

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Рост внутренней энергии кварца, находящийся в зависимости от времени измельчения установили путем измерения экзотермического эффекта при ДТА. Приведенная энергия выделяется при последующем нагревании кварца.

Из сопоставления отдельных измерений следует, что выделение энергии начинается в интервале температур 110±10 °С и достигает нескольких пиков. Первый пик, проявляющийся именно у проб с небольшим временем измельчения при температуре 325±15°С в зависимости от времени измельчения смещается в приведенном интервале к более низкой температуре. Второй пик, значение которого растет с временем измельчения, получается при температуре 420±20 °С, а третий пик при температуре 540±10 °С в зависимости от времени измельчения перекрывается вторым пиком.

Рост внутренней энергии кварца вызывается образованием свободных радикалов, или ионов появляющихся в расщепленных поверхностях и трещинах кристаллов кварца. Это доказано тем, что величина повышенной внутренней энергии кварца растет в присутствии интенсификатора помола (поверхностно активных веществ), мешающего приближению частиц до расстояния действия межмолекулярных сил и в результате того и их агломерации и исчезанию свободных радикалов на поверхности частиц. Однако рост внутренней энергии свидетельствует о том, что основная энергия для измельчения израсходуется на разрушение химических, поляризуемых связей Si—O. Мнение о том что внутренняя энергия кварца растет с образованием свободных радикалов и в зависимости от механизма помола, доказано тем, что рост энергии проявляется даже при измедьчении аморфного вещества, как например кварцевого стекла, где однако отдельные тетраэдры SiO_4^{4-} не находятся в стройном упорядочении, а они только взаимно связаны. В таком случае имеется для любого времени измельчения в сущности только один пик при температуре 340±15 °С. Начало и конец действия подобны кварцу.

Кроме того приводится методика, служащая для определения внутренней энергии твердых веществ при измельчении.

Рис. 1. Зависимость поверхности пика чистого кристобаллита от скорости нарастания температуры при ДТА.

Рис. 2. Зависимость величины коэффициента восстановления от скорости нарастания температуры при ДТА.

Рис. 3. Зависимость скорости нарастания температуры от температуры при ДТА кварца.

Рис. 4. График калибрации. Зависимость поверхности пика (ΔP) [отн. см²] и количества соответствующего выделившегося тепла (ΔQ) [кал/г] при ДТА от содержания кристобаллита.

Рис. 5. Кривая ДТА кварца после обработки в ступке.

Рис. 6. Кривая ДТА смеси кварца и кристобаллита после обработки в ступке.

Рис. 7. ДТА кварцевого песка, измельчаемого 30 минут: Δt: a — первый нагрев, b — второй нагрев той же пробы, t — нарастание температуры в зависимости от времени.

Рис. 8. ДТА кварцевого песка, измельчаемого 60 минут: Δt : a — первый нагрев, b — второй нагрев, c — третий нагрев той же пробы, t — нарастание температуры в зависимости от времени.

Рис. 9. ДТА кварцевого песка, измельчаемого 120 минут: Δt : a — первый нагрев, b — второй нагрев той же пробы, t — нарастание температуры в зависимости от времени.

Рис. 10. ДТА кварцевого песка, измельчаемого 240 минут: Δt : a — первый нагрев, b — второй нагрев той же пробы, t — нарастание температуры в зависимости от времени.

Рис. 11. Зависимость приращения внутренней энергии кварца от времени измельчения: ΔP — поверхность пика, приводимая к скорости 19 °С/мин., ΔQ — нарастание внутренней энергии кварца.

Рис. 12. Зависимость нарастания свободной энергии кварца от времени и условий измельчения: 1 — без интенсификатора помола, 2 — с интенсификатором помола 0,5 % этилового спирта, денатурированного метиловым спиртом и 0,5 % концентрированного аммиака.

Рис. 13 ДТА кварцевого стекла, измельчаемого 10 минут в вибрационной мельнице: t — температура, Δt: a — различие температуры при первом нагреве, b — различие температуры при втором нагреве той же пробы.