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THERMAL EFFECTS OF CONTAMINATION, ADSORBED WATER AND ANNEALING ON THE DTA OF POWDERED QUARTZ

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During the grinding of quartz, water is adsorbed from the atmosphere, but this water gave no detectable thermal effect on DTA because it was evolved uniformly up to 1000°. However, in conjunction with an iron contaminant, the adsorbed water was involved in an oxidation reaction causing noticeable thermal effects for quartz powdered in a vibration mill constructed of steel parts. When powdered so finely that the $\alpha-\beta$ inversion peak at 573° had disappeared, annealing caused a partial redevelopment of the peak but recrystallization of disrupted quartz was too small an effect to give any detectable exothermic peak on DTA.

We reported previously [1, 2] that when quartz was ground for several hundreds of hours, the disappearance of the $\alpha-\beta$ inversion peak on DTA was caused not by conversion of the quartz to an amorphous phase of silica, but by the formation of a microcrystalline variety of quartz with modified $\alpha-\beta$ inversion characteristics. A dispersion of the inversion over a range of temperature was suggested [1], and therefore when thermal effects were observed outside the range of temperature where the $\alpha-\beta$ inversion normally occurs, these were investigated and are reported here. Although the research was mainly concerned with the effect of grinding on the $\alpha-\beta$ inversion, the findings reported in the present paper relate chiefly to the additional thermal effects of adsorbed water and contamination which occur during grinding.

Contrasting with the $\alpha-\beta$ inversion which occurs on every heating, the liberation of adsorbed water or the oxidation of contaminants, if taken to completion during the first DTA run on a given sample, will not produce thrmal effects or a second or subsequent DTA test. However the possible release of stored grinding energy involving the recrystallization of disrupted surface layers on the particles of quartz, discussed by Lindström [3], must be considered. Any broadening of the $\alpha-\beta$ inversion should produce effects, if observeable, both on the initial DTA and subsequent DTA tests of a given sample, unless annealing reduces the strains within the particles to give a sharpening of the $\alpha-\beta$ peak [2].

The thermal effects described in this paper are often very small but, nevertheless, they are real in the sense of being reproducible, both on repeated DTA tests and, except in the case of the anomalous effects reported, from one milling test to another involving quartz from various sources. The interpretation of such small

thermal effects may appear more difficult to the reader since, for publication, the curves have been reduced to about one quarter of the original size.

Definition. In this paper an 'initial' DTA curve is one obtained for a given sample not previously heated; a 'reheat' DTA curve refers to a second or subsequent test on the given sample after the initial DTA experiment.

Results

Quartz powdered in a steel vibration mill

A quartz sand from Chatteris, Cambridgeshire was milled for various durations up to 400 hours in a vibrating steel chamber containing steel balls. Samples from this mill were grey, due to iron contamination, but after an initial DTA the samples had turned brown due to oxidation by the air. A Stanton 625 apparatus was used

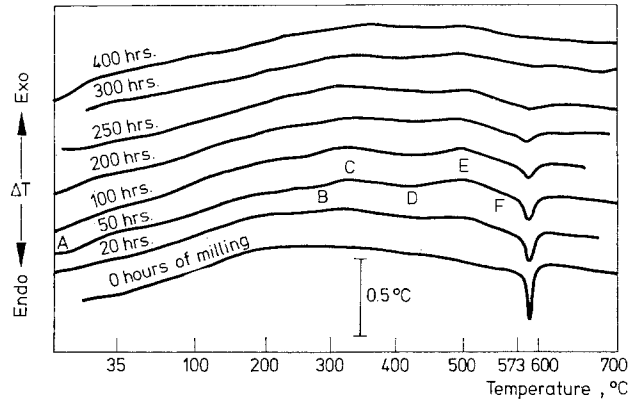

Fig. 1. Initial DTA curves for quartz milled for various times in a steel vibration mill

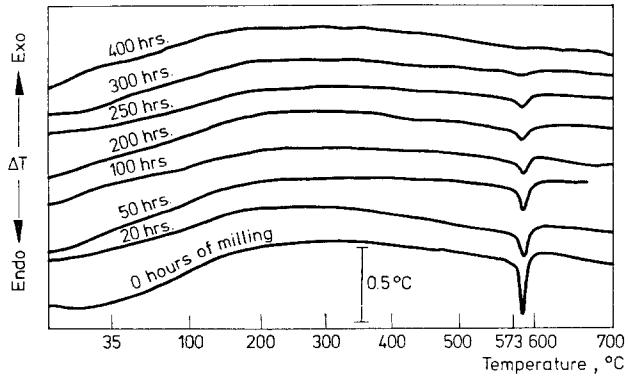

Fig. 2. Reheat curves for the same samples from Fig. 1

with alumina reference material, 0.285 g of sample, and a heating rate of 10°/min. The initial DTA curves in Fig. 1 contained fluctuations in addition to the inversion peak at 573°, which have been labelled *BCDEF* for the quartz milled 50 hours. In spite of the oxidation of the iron contaminant, the samples lost weight during the initial DTA due to the evolution of adsorbed water. The same samples, when reheated, gave much smoother curves (Fig. 2) and did not change weight which suggested that both the oxidation of iron contaminant and the evolution of adsorbed water has been taken to completion during the initial DTA.

A comparison between the initial and reheat curves of Figs 1 and 2 suggested that the fluctuations *BCDEF* could have consisted of exothermic peaks *BCD* and *DEF*, or of an endothermic peak *CDE*. Since we knew that both exothermic and

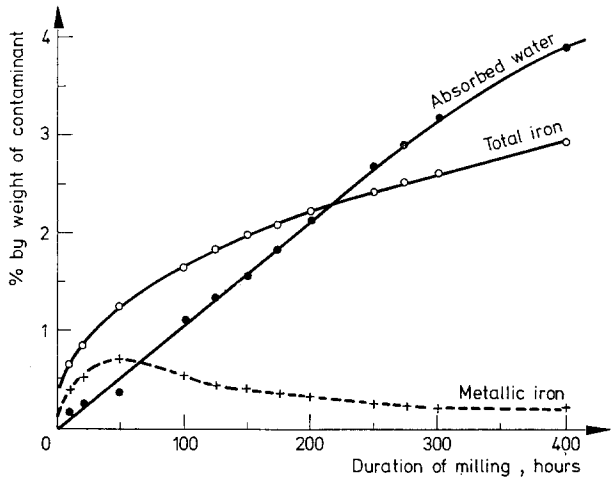

Fig. 3. Percentages by weight of water, total iron and metallic iron as a function of duration of milling of the quartz

endothermic effects were taking place during the initial DTA, viz. oxidation of the iron and release of adsorbed water, a combination of these two effects might have produced such a DTA curve. The superimposition of reheat curves upon the initial curves did not resolve whether the fluctuations were exothermic or endothermic, because random drifts from one test to another prevented a close comparison.

Small fluctuations are not easy to quantify, but they appeared larger in magnitude for the quartz samples milled for 50 and for 100 hours than for the quartz milled for 400 hours. This suggested a possible linkage with the oxidation of metallic iron contaminant which increased to a maximum around 50 and 100 hours of grinding rather than with adsorbed water which increased continuously during grinding; Fig. 3 gives details of quantities of iron and adsrobed water for the various durations of milling. The reason for the decrease in quantity of metallic iron during grinding from 100 to 400 hours was that grinding converted the metal

to iron(II)-iron(III) oxide (Fe_3O_4) and further contamination was mostly in the form of this oxide [4].

Another argument against adsorbed water causing the fluctuations seen on the initial DTA is that the water was evolved not only over the range of temperature corresponding with *CDE* of Fig. 1 but from room temperature to well above the inversion temperature. Thermogravimetric data is given in Fig. 4 indicating that any endothermic effect, resulting from the evolution of water, would probably take the form of a drift over the whole curve rather than just over the range *CDE* in Fig. 1. In no case, however, was such a drift detected, presumably because the heat is absorbed over such a wide range of temperature that, at any given moment, the deflection of the DTA curve is only very small, and generally less than the random fluctuations which occur from one test to another.

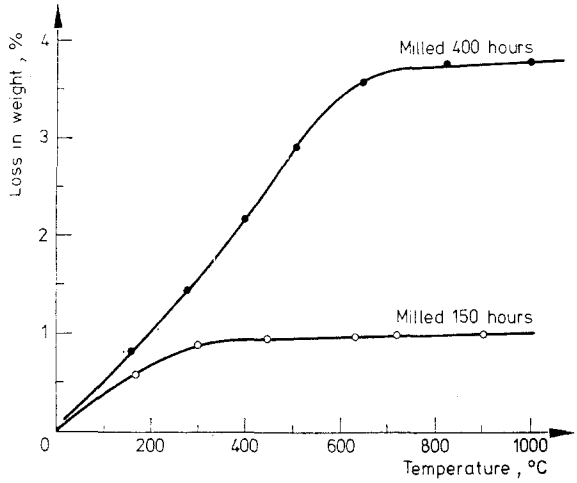

Fig. 4. Thermogravimetric data for quartz milled 150 and 400 hours

The extraordinary fact to emerge, however, was that neither the oxidation of the iron contaminant nor the evolution of the adsorbed water, if constrained to take place separately, gave rise to any thermal effects detectable by DTA. By performing DTA in nitrogen or grinding the quartz in a mill constructed of agate, it was possible to obtain data relating to thermal effects of iron oxidation and adsorbed water evolution separately.

DTA in nitrogen

The quartz milled for 100 hours in the steel vibration mill was subjected to an initial DTA in nitrogen gas, thus suppressing the oxidation of the iron but permitting the water to be evolved. Curve 1, Fig. 5 was obtained, in which the fluctuations had been suppressed as would be expected if iron oxidation had been the cause of

the fluctuations seen in Fig. 1. However, when the sample was reheated in air to permit oxidation giving curve 2, Fig. 5, only a very small fluctuation BCD was observed, in spite of the sample changing colour from grey to brown, and increasing in weight by the expected amount for a complete oxidation of the iron contaminant.

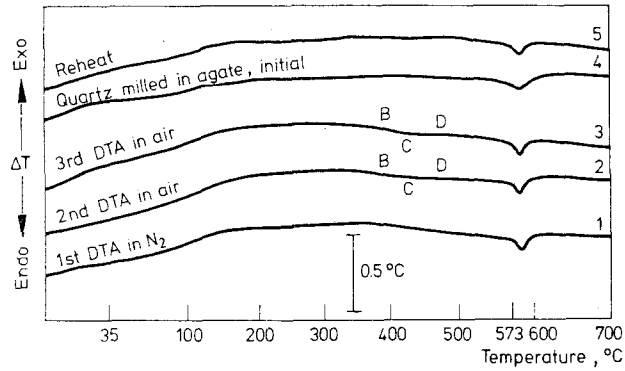

Fig. 5. Initial DTA in nitrogen for quartz milled 100 hours, showing a suppression of the fluctuations although water was liberated. A second heating in air permitted iron oxidation but fluctuations did not appear. The slight peak BCD was perhaps associated with the $\alpha-\beta$ inversion. Curves 4 and 5 show how quartz milled in agate may liberate 3%wt. water during initial DTA without producing noticeable fluctuations

This very small fluctuation labelled BCD on curve 2, Fig. 5, was not related to the oxidation of the iron because the fluctuation reappeared when the sample was heated for a third time in air giving curve 3, Fig. 5, whereas the iron had been completely oxidized on the previous heating. We have observed this effect on many DTA curves for quartz from various sources milled in both steel and agate mills, but since the effect was very small, a systematic investigation would have been difficult to perform. It would certainly be interesting to know if this fluctuation, which occurred on repeated DTA heatings, was related to, or a part of, the $\alpha-\beta$ inversion.

The suppression of the fluctuations of the type seen in Fig. 1, when the initial DTA was carried out in nitrogen, probably rules out the exothermic release of stored grinding energy as a cause, because the recrystallization of disrupted quartz should occur irrespective of the atmosphere in which the quartz is heated.

Quartz milled in an agate vibration mill

Quartz powdered in a mill constructed of agate parts could theoretically be very different from that comminuted in a mill constructed of steel parts. This is because iron increases the affinity of silica for water [5] so apart from the absence of iron there could well be much less adsorbed water involved. Impurities can also influence the inversion [6], and moreover grinding in an agate mill will not only

result in a purer product, but also, being less dense than steel, might not cause such severe damage to the quartz and modification of the $\alpha-\beta$ inversion.

However, during a 100 hour grind of the quartz from Chatteris in an agate mill, a comparable reduction in size of the $\alpha-\beta$ peak occurred and a greater adsorption of water from the atmosphere was obtained. Curves 4 and 5, Fig. 5 are the initial and reheat DTA tests on this sample, and although 2.94% wt. water was evolved during the initial DTA, no noticeable fluctuations were caused. No significant drift could be detected on any of the initial DTA curves for quartz milled in agate mills, when compared with the corresponding reheat curves. This confirmed that the evolution of water in the absence of iron gave no detectable thermal effects on DTA, and this appeared to be generally true for some hundred tests involving quartz milled in agate mills in our laboratory.

An anomalous DTA peak seen in a quartz oscillator plate

Quartz sand is not a particularly pure source of quartz and surface impurity already present might find its way into the lattice during grinding to cause a modification of the inversion. Questions were also raised in our research concerning the milling together of the two enantiomorphs of quartz, left and right-handed, as

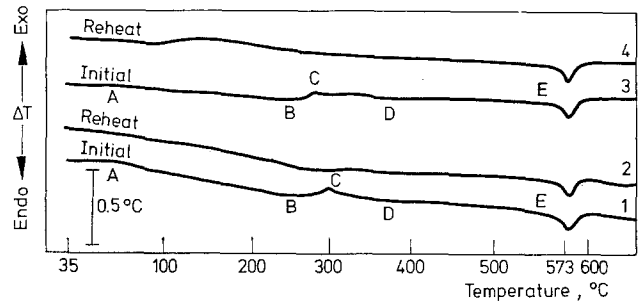

Fig. 6. An anomalous reaction given by a single quartz crystal ground for 100 hours in the agate mill

a sand consists of approximately equal proportions of both. Therefore several investigations were performed on single crystals of quartz obtained from the electronics industry.

A 500 khz AT cut natural quartz blank, was crushed in a fly-press, and washed in hydrochloric acid. DTA at 8.33°/min gave no differences between initial and reheat curves for this sample, but when ground in the agate mill for 100 hours, unusual peaks appeared on the initial DTA curves. Curves 1 and 3, Fig. 6 are initial curves, and curves 2 and 4 are the corresponding reheat curves for two samples obtained from the mill. We cannot provide any explanation for this abnormal peak; if it is an exothermic peak *BCD* as opposed to endothermic (*ABC* and *CDE*) then this is the closest we have come to observing the release of stored grinding

energy, as discussed by Lidström [3]. If caused by the latter effect, however, it should have been observable in every case and not just occasionally; therefore the peak seems to be associated with some anomaly in the quartz.

Annealing of powdered quartz

A single crystal (25 g) of *z*-cut left-handed Brazilian quartz was checked for the absence of twins, crushed in a fly-press and washed in hydrochloric acid, and a starting material of less than 12 mesh was prepared. Curve 1, Fig. 7 gives the DTA of this starting material at a heating rate of 12°/min. After 470 hours grinding in

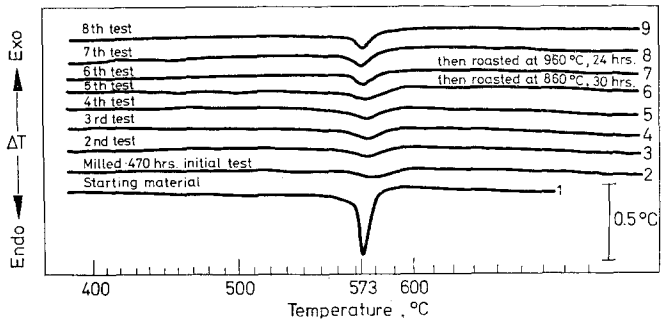

Fig. 7. A single crystal of quartz milled for 470 hours in an agate mill showing regrowth of the $\alpha-\beta$ inversion peak after repeated DTA and annealing treatments. A slight change of inversion temperature after grinding is also noticeable but recovers during annealing to the original inversion temperature

the agate mill the $\alpha-\beta$ peak seen in curve 2 had become much reduced, and in this particular case the peak appears to have increased in temperature a few degrees after the grinding. Curves 3, 4 and 5 were for repeated heatings going to a maximum temperature of 750°, and the inversion peak showed some redevelopment and tendency to return to the same inversion temperature as the starting material. After curve 6, the sample was roasted for 30 hours at 860°, (i.e. just below the equilibrium temperature between quartz and tridymite), and then curve 7 was obtained. A further roasting at 960° for 25 hours preceded the curves 8 and 9, causing a further redevelopment of the $\alpha-\beta$ peak.

Discussion

The redevelopment of the $\alpha-\beta$ peak in powdered quartz, caused by annealing, indicates that grinding does not reduce the size of the $\alpha-\beta$ peak through the action of diffusion of surface contaminants into the quartz. If impurities formed a solid solution and a spreading of the $\alpha-\beta$ inversion over a range of temperature, then

annealing would enhance the diffusion to bring about a further reduction of the $\alpha-\beta$ inversion peak, whereas annealing caused a regrowth of the peak. Although Malov and Sonyushkin [7] has found that repeated cycling through the inversion removed impurity atoms from structural positions, we cycled only a few times through the inversion and so the $\alpha-\beta$ peak regrowth seemed more associated with annealing than with cycling through the inversion.

The redevelopment of the $\alpha-\beta$ peak implies that whatever effects are caused by the grinding process, these are, to some extent, removable by annealing the powdered quartz. It is inconceivable that annealing at temperatures well below melting could cause the recrystallization of separate particles into single crystals in anything less than thousands of years: therefore the effect of the annealing must be to remove damage from within the individual particles perhaps in the form of strain, Dauphiné twinning and microcracks, or of the disrupted form described by Lidström. It is interesting that the specific surface of the powder, measured by photo-extinction, levelled off after 100 hours of milling to a value of 2.7 m^2/g whereas the milling from 100 to 400 hours was accompanied by a continued adsorption of atmospheric moisture. This suggested that, under our conditions of milling, the first 100 hours of grinding causes the production of separate particles but grinding from 100 to 400 hours introduces damage such as microcracks not sufficiently severe to cause fracture into separate particles. It is this latter kind of damage which is presumably influenced by annealing.

Conclusions

The fluctuations observed on initial DTA for quartz milled in the steel vibration mill were due to a combination of metallic iron oxidation and liberation of adsorbed water taking place simultaneously. The oxidation of the iron contaminant in the absence of the evolution of adsorbed water from the quartz, or vice versa, did not normally cause any noticeable thermal effects, under our conditions of milling and DTA. A certain amount of damage was removable by annealing the powdered quartz, producing a redevelopment of the $\alpha-\beta$ inversion peak, but the release of such energy stored as damage did not normally cause any exothermic effects observeable on DTA in our research.

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References

1. G. S. M. Moore and H. E. Rose, Nature, 242 (1973) 187.
2. G. S. M. Moore and H. E. Rose, Nature, 253 (1975) 525.
3. L. Lidström, Acta Polytechnica Scandinavica, Chemistry including Metallurgy Series Ch. 75.

4. G. S. M. MOORE, J. Phys. E., 6 (1973) 1170.
5. J. A. HOCKEY, Chem. Ind., 1 (1965) 57.
6. M. L. KEITH and O. F. TUTTLE, Amer. J. Sci., Bowen vol. (1952) 203.
7. YU. V. MALOV and V. E. SONYUSHKIN, Sov. Phys. Cryst., 20 (1976) 644.

RÉSUMÉ — Lors du broyage du quartz, il se produit une adsorption de l'eau atmosphérique mais cette eau ne donne pas d'effet thermique décelable par ATD car elle se dégage régulièrement jusqu'à 1000°. Cependant, en présence de fer comme contaminant, l'eau adsorbée intervient dans une réaction d'oxydation qui donne des effets thermiques perceptibles dans le cas de quartz pulvérisé dans un vibrobroyeur en acier. Si le quartz est en poudre assez fine pour que le pic d'inversion $\alpha-\beta$ à 573° disparaisse, le recuit provoque la réapparition partielle du pic. La recristallisation du quartz est cependant trop faible pour donner un effet exothermique décelable par ATD.

ZUSAMMENFASSUNG — Während des Vermahlens von Quartz wird Wasser aus der Atmosphäre adsorbiert, jedoch ergab dieses Wasser keinen nachweisbaren thermischen Effekt in der DTA, da es bis zu 1000° gleichmässig freigesetzt wird. Im Zusammenhang mit einer Eisen-Verunreinigung wurde jedoch das adsorbierte Wasser in eine Oxidationsreaktion einbezogen, welche beim in einer aus Stahlteilen gefertigten Vibrationsmühle zerpulvertem Quartz nachweisbare thermische Effekte verursachten. Wenn so fein pulverisiert wurde, daß der $\alpha-\beta$-Inversions-Peak bei 573° verschwunden war, verursachte eine Wärmebehandlung eine teilweise Wiederentwicklung des Peaks, jedoch war die Rekristallisation des zerstörten Quartzes zu geringfügig um einen nachweisbaren exothermen Peak in der DTA-Kurve zu ergeben.

Резюме — Во время измельчения кварца из атмосферы адсорбируется вода, которая не дает определяемого с помощью ДТА термического эффекта, поскольку равномерно выделяется вплоть до 1000°. Однако находясь совместно с примесью железа, адсорбированная вода включается в окислительную реакцию, вызывая заметные термические эффекты в порошкообразном кварце в вибромельнице из стали. В случае очень мелкого порошка $\alpha-\beta$ пик инверсии при 573° исчезал, однако отжиг вызывал вновь частичное появление пика, но рекристаллизация деструктированного кварца была настолько малой, чтобы дать какой-либо регистрируемый экзотермический пик в ДТА.