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Thermal shock of quartz lascas

H. IWASAKI*, D. TORIKAI
Laboratório de Quartzo, Departamento de Materiais, Faculdade de Engenharia Mecânica, UNICAMP, 13100 Campinas, São Paulo, Brasil

As a pre-treatment to grinding, quartz lascas (crushed pieces) were thermally shocked into room-temperature water by quenching from temperatures between 50 and 800 °C. Comminuted particles exhibited two distinctive geometries, granular for T_q(quench) $< T_c$ (573 °C) and needle-like when $T_q > T_c$. The needle-like shapes become thinner and longer with increasing temperature above T_c. The differences in shape are believed to result from the differences in the crack generation patterns which are governed by the thermoelastic properties in the α-phase and β-phase of the quartz during the thermal shock process. Crack densities induced by the thermal shock were measured as a function of T_q. For the temperature range of $\sim 200\,°C < T_q < T_c$ and $T_c < T_q < \sim 800\,°C$, the resulting crack densities were determined to be governed by the rate of crack nucleation, which is characterized by an Arrhenius-type equation. The activation energies associated with the crack nucleation rates for the two regions were determined to be 14 and 39 kJ mol^{-1}, respectively.

1. Introduction

Basic studies of the comminution of minerals involving quartz have a long history. In 1930, Gross and Zimmerley [1–3] addressed the method of surface measurement for crushed quartz which had been previously classified by sieves and studied the relation of the work-input to the surface area produced. Axelson and Piret [4] and Axelson *et al.* [5], in 1950 and 1951, respectively, reported the crushing of single quartz particles and concluded that the main problems were concerned with (i) the mechanism of the fracture process itself, (ii) the particle size distribution of the crushed product, and (iii) the relationship between the work or energy input and the new surface area produced. Theoretical derivations of comminution distribution equations for single and repeated fractures have been presented by Gaudin and Meloy [6, 7]. Continuous grinding in a small wet ball mill was studied in detail by Kelsall *et al.* [8–11], while recently, Kanda *et al.* [12] and Yashima *et al.* [13] have studied grinding and crushing from the viewpoint of fracture mechanics. In addition to these basic studies, some general aspects of mineral crushing on an industrial scale have been considered by Lynch [14].

At the present, quartz powder assumes an important role as the raw material to produce vitreous (fused) silica, other glasses, many engineering ceramics, semiconductor devices, etc. A significant fraction of that quartz powder is produced from natural quartz resources for which Brazil is a principal supplier. Several companies in Brazil are producing quartz powder of conventional grades utilizing natural quartz from various mineral deposits.

Until recently, no extensive studies of the characteristics and properties of the "comminution" and the "powdering" processes of Brazilian quartz have been completed. Therefore, the present research was performed to increase the fundamental understanding of the process of quartz powder production, considering the present and future conditions of quartz powder production in Brazil. Approaches different from the standardized procedures described in the literature were adopted for this study of the thermal shock-assisted fracturing and powdering of quartz.

This research consists of three related studies: (i) the characterization of crack patterns induced by thermal shock quenching of quartz, (ii) the influence of ball milling conditions on the powder production, and (iii) characterization and simulation of the grain size distribution in the resulting quartz powder. It is of special interest that the characteristics of the powdering process are markedly influenced by the crack patterns induced by the thermal shock quenching which is employed as a pre-treatment process for the quartz to be powdered by milling.

In the present research, the characterization of crack patterns induced by thermal shock quenching is described in detail.

2. Experimental procedure

2.1. Quartz lasca as a raw material for powder production

A large volume of quartz known as *lasca* is produced in Brazil. The word lasca means piece, chip, or fragment in Portuguese. Here, the term lasca refers to a

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* *Present address*: Sobudai-Danchi 1-6-15-12, Sagamihara 228, Japan.

crushed piece of quartz crystal (10–30 g each). Usually, lascas are produced by hammering by hand from large blocks of quartz of less than piezoelectric quality, or from the rock-like blocks which are without obvious crystal facets. The lascas are usually classified by visual inspection of their transparency and graded as "1st", "Mix", "2nd", etc., without criteria based on either physical or chemical measurements.

In the present research, lascas were obtained from a quartz deposit located in Cristalândia, Tocantins, Brazil. They had been graded as "2nd" class, which means having "low contents" of inclusions and microcracks. The transparency is influenced mainly from the presence of inclusions and microcracks. Lascas with weights in the range from about 10 to 25 g were chosen and used throughout the present work. The shapes of these lascas may be regarded as nearly equiaxed or sphere-like, rather than cubes or cylinders, although their shapes are often irregular because of the hammering. The equivalent diameters of these lascas were estimated to be about 2–2.5 cm.

2.2. Thermal shock fracture of lascas

To introduce artificial cracks as a pre-treatment before powdering, the lascas were first thermal shock-quenched from various temperatures into distilled water at room temperature, $T_r(\sim 30\,^{\circ}\mathrm{C})$. Thermal shock quenching temperature, T_q values, were chosen between 50 and 800 °C. Lascas heated at the chosen temperatures for quenching were rapidly transferred from the electric furnace into the adjacent water bath. The crack densities and patterns of these artificially induced cracks influence various characteristics of the powdering process and assume a useful role to increase the efficiency of the comminution.

It is well known that thermal shock-induced stresses depend on the size and shape of the material [15]. Thermal stress for the case of spherical shapes has been analysed in detail [16, 17]. As the shapes of these lascas are considered to be approximately spherical, rather than cubic or cylindrical, although their shapes are usually irregular, the spherical analysis can be applied. In addition, quartz is anisotropic in its elastic and thermal properties. To simplify the analyses, the influence of the irregularity in shape was ignored in the analyses of thermal stress. Evaluations of the critical temperature differential and thermal stresses during quenching in the quartz lascas were performed as though it were an isotropic material.

3. Result and discussion

3.1. Characteristics of surface crack generation by quenching

During the thermal shock quench, the surface of the lasca is subjected to a biaxial tensile thermal stress. There exists a critical temperature differential, $\Delta T_c = T_q - T_r$, which causes extension or growth of surface cracks from the pre-existing surface flaws. Further cracking occurs when the thermal stress induced by the temperature differential, $\Delta T > \Delta T_c$, exceeds the fracture stress.

Surface crack densities induced by the thermal shock quench were measured as a function of the quenching temperature, T_q. The crack density was defined as the averaged number of cracks across the unit length (1 cm) at three randomly chosen points on the lasca surface after quenching. Cracks were observed and counted under an optical microscope and in those cases of high crack density, evaluation was made with the aid of photomicrographs.

The relationship between the crack density, $N(\mathrm{cm}^{-1})$, and the quenching temperature T_q is shown in Fig. 1. The influence of quenching temperature on the thermal shock-generated crack density can be divided into three distinct regions:

$$T_q < \sim 200\,^{\circ}\mathrm{C} \text{ (region I)}$$

$$\sim 200\,^{\circ}\mathrm{C} < T_q < \sim 600\,^{\circ}\mathrm{C} \text{ (region II)}$$

$$\sim 600\,^{\circ}\mathrm{C} < T_q \qquad \text{(region III)}$$

The temperature of the boundary between region II and region III corresponds closely with the α–β phase transition temperature, T_c (573 °C), of quartz.

The cracks which are induced by thermal shock quenching grow further towards the centre of the lasca body with increasing quenching temperature. Those lascas quenched from temperatures higher than about 500 °C are readily crushed between one's finger tips. Those lascas which are crushed between the finger tips have specific geometrical shapes which depend on the quenching temperature. Crushed lascas which are quenched from temperatures below T_c exhibit granular shapes. However, the crushed lascas show needle-like shapes when they have been thermally shocked from temperatures higher than T_c. The needle-like shapes become thinner and longer with an increase of

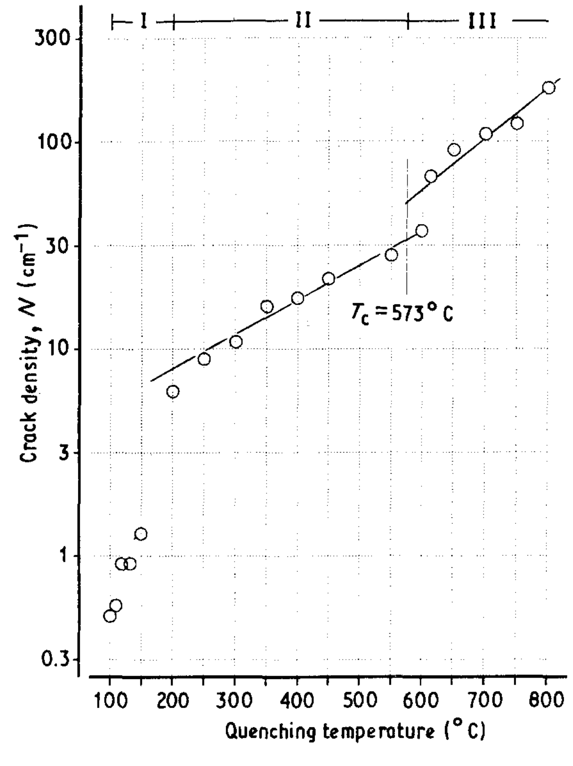

Figure 1 Crack densities as a function of the quenching temperature.

T_q above T_c. The two geometries are shown in Fig. 2a and b.

Cracks observed in the cross-sections of lascas quenched from region III, above T_c, show a pattern of focusing isotropically towards the body centre from the surface of the lasca. In other words, the thermal shock cracks have a radiative pattern, isotropically towards the surface from the centre of the lasca. These observations suggest that for quenching from region III, cracks principally grow in radial directions during the thermal shock time in which the quartz lascas are in the β-phase during the quenching process.

The granular equiaxed fractured grains that are shown in Fig. 2a which result from thermal shock quenching below T_c are fully consistent with the fracture toughness measurements of α-quartz by Iwasa and Bradt [18]. The lack of any specific geometric form of these granules is indicative of the near equality of the fracture toughness of α-quartz on all of the planes which have been measured, about 0.85 to 1.1 $\mathrm{MPa\,m^{1/2}}$. Of course, as demonstrated by Iwasa and Bradt, this is exactly why α-quartz usually exhibits a conchoidal fracture surface instead of the pronounced planar cleavages which are experienced by many other single crystals. By contrast, in Fig. 2b the resulting grains have a distinctive geometric form, one that is representative of cleavage fracture on specific crystal planes. It is obvious that the two different resulting fragment shapes (Fig. 2a versus Fig. 2b) are the consequence of the fracture processes originating and proceeding in different crystal structures.

The geometric shape of the individual grains in Fig. 2b is suggestive of a form representative of hexagonal crystals. It may be expected as β-quartz is hexagonal. Although the cleavage toughnesses of β-quartz have not been reported, the grain shapes in Fig. 2b strongly suggest that the structure may be expected to readily cleave on the prism planes, perhaps both the $\{10\bar{1}0\}$ and the $\{2\bar{1}\bar{1}0\}$ types. Basal and rhombohedral cleavages may be secondary in that hexagonal structure is evidenced by some of the ends of the prisms. Although this may be somewhat speculative, there is no disputing the shape differences between the resulting fragments from fracture below and above T_c, as depicted in Fig. 2a and b.

3.2. Critical temperature differential, ΔT_c

The relation between the critical quenching temperature differential, ΔT_c, and the average tensile strength, σ_f, is well established [15, 19, 20] :

$$\Delta T_c = \frac{\sigma_f(1-\nu)}{\alpha E A} \tag{1}$$

where ν, α and E are, respectively, Poisson's ratio, the coefficient of thermal expansion and Young's modulus of the material. A is a number between 0 and 1 and is known to be a function of Biot's modulus. To estimate ΔT_c for the present case, it is necessary to obtain values of σ_f, ν, α and E of α-quartz when A is assumed to be unity.

The fracture toughness of the principal planes for several crack growth directions of α-quartz at room temperature has been evaluated to be 0.9 $\mathrm{MPa\,m^{1/2}}$ as an average [18, 21]. From this value, the bending strength is estimated to be about 78 MPa [18]. For most materials, the bend strength exhibits higher values than the tensile strength and is roughly twice the

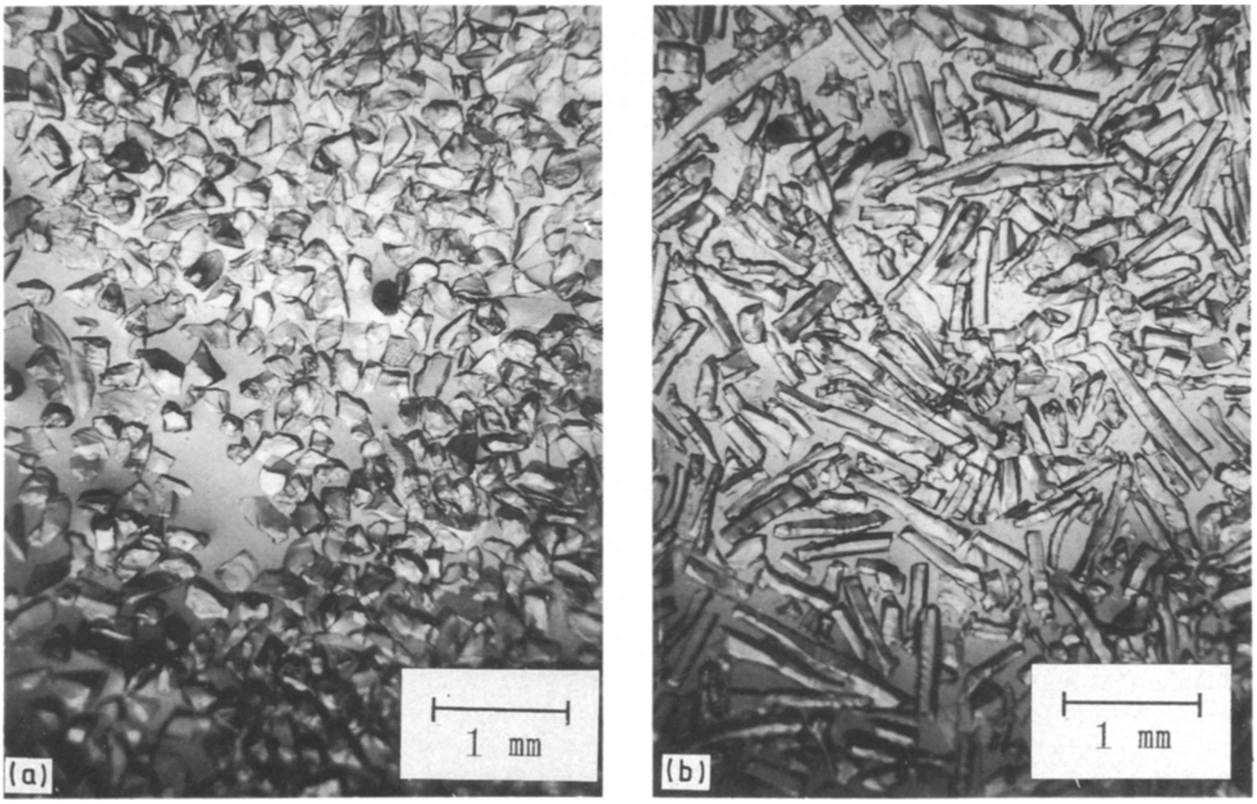

Figure 2 (a) Granular particles from lascas quenched from 500 °C, (b) needle-like fragments from lascas quenched from 700 °C.

tensile strength in the case of many engineering ceramics [19, 22]. Therefore, the tensile strength of α-quartz is estimated to be about 40 MPa.

Poisson's ratio can be defined as [23, 24]

$$\nu = -(S_{12}/S_{11}) \quad (2)$$

where S_{12} and S_{11} are compliance constants. From this relation, the Poisson's ratio of α-quartz is estimated to be 0.14. The value of α is estimated to be $10^{-5}\,^{\circ}\mathrm{C}^{-1}$ as an average of a_{11} and a_{33}. Young's modulus, E, of α-quartz has considerable anisotropy. It ranges between 70 and 130 GPa [21, 23]. For the case of quartzite, specific values of these constants have been evaluated as follows [25]:

$$E = 97\,\mathrm{GPa} \qquad \nu = 0.15 \qquad \alpha = 10.6 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$$

By using the above, an α of $10^{-5}\,^{\circ}\mathrm{C}^{-1}$, a ν value of 0.15, a Young's modulus of 100 GPa and an average tensile strength of 40 MPa, a ΔT_c of $\sim 34\,^{\circ}\mathrm{C}$ is obtained by assuming $A = 1$, which means infinitely rapid quenching. As shown in Fig. 1, the first observable cracks from quenching occur at about a T_q near 100 °C.

At low temperatures T_q, the heated lascas do not cause the water to boil and heat transfer occurs slowly by convection. If A is assumed to be 0.5 because of slow cooling, then a ΔT_c of $\sim 68\,^{\circ}\mathrm{C}$ is obtained. From these estimations, it may be interpreted that the temperature, 100 °C, as T_q under the water bath ($\sim 30\,^{\circ}\mathrm{C}$) corresponds to the critical temperature for the growth or extension of those cracks which exist on the lasca surfaces before quenching. Therefore, Region I can be regarded as a region where cracks existing on the lasca surface grow or extend under the influence of the thermal stresses induced by quenching.

3.3. Crack generation characteristics in regions II and III

The thermal stress, σ_{th}, to extend cracks in region II can be calculated by using the specific values of the material properties from section 3.2. It is presented as a function of ΔT by

$$\sigma_{\mathrm{th}}(\mathrm{MPa}) = 1.18\Delta T(^{\circ}\mathrm{C}) \qquad \Delta T > \Delta T_c \quad (3)$$

except for the region near to T_c. Here, A is assumed to be unity because of the "high temperature" region.

From data shown in Fig. 1, the relation between the crack density N_{II} (cm^{-1}) in region II and the quenching temperature differential ΔT is approximated by the linear relationship

$$N_{\mathrm{II}} = N_0 + N_1 \Delta T(^{\circ}\mathrm{C}) \quad (4)$$

In the temperature range of T_q from 200 to 500 °C, N_0 and N_1 are evaluated to be $-4.95\,\mathrm{cm}^{-1}$ and $0.063\,\mathrm{cm}^{-1}\,^{\circ}\mathrm{C}^{-1}$, respectively, with a correlation, r^2, of 0.992. Applying the condition that $N_{\mathrm{II}} = 0$ yields a critical temperature differential, $\Delta T_i(^{\circ}\mathrm{C})$, for crack initiation that is equal to 78.6 °C. This value agrees favourably with the value of ΔT_c ($\sim 68\,^{\circ}\mathrm{C}$) obtained from the fracture characteristics under the assumption that $A = 0.5$.

In region III, quartz is initially in the β-phase which has hexagonal symmetry. The adiabatic elastic compliances, S_{ij}, of the β-phase have been measured by Kammer *et al.* [26] from 580 to 800 °C. Young's modulus, E, of the β-phase can be calculated from the relation [27]

$$E = [S_{11}(1 - \cos^2\gamma)^2 + S_{33}\cos^4\gamma + (2S_{13} + S_{44})(1 - \cos^2\gamma)\cos^2\gamma]^{-1} \quad (5)$$

where γ is an angle measured from the c axis, the [0001]. Angular-dependent characteristics show that, from 600 to 800 °C, the Young's modulus only varies from 93 to 115 GPa. It exhibits much less elastic anisotropy than α-quartz. Poisson's ratio is calculated to be 0.063, 0.101 and 0.115 at 600, 700 and 800 °C, respectively. The thermal expansion of quartz was measured by Jay [28] from 18 to 730 °C. His data reveal that the expansion increases rapidly as the temperature approaches T_c and exhibits an abrupt change followed by a contraction in the β-phase. From his data for the β-phase, the coefficients of "contraction" parallel and perpendicular to the c axis are evaluated approximately to be -1.6×10^{-6} and $-0.86 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$, respectively. The thermal behaviour of β-quartz was recently reconfirmed by Kihara [29].

It is evident that during the quenching process, the characteristics of the thermal stresses within the β-phase are very different to those which develop in the α-phase. In addition, it is well known that cracks may be generated as a consequence of the attendant volume change when quartz crystals pass through the α–β inversion [30]. If the crack generation induced by quenching from a T_q in the β-phase is governed by the change of volume at T_c, then the crack patterns may be independent of T_q in the range higher than T_c. However, the observed results depicted in Fig. 1 are that the crack density N_{III} increases exponentially with increasing quenching temperatures above T_c. This suggests that the process of crack initiation must be completed during the brief time period when the heated quartz lascas are in the β-phase. The specific characteristics of the crack initiation in region III may be attributed to the elastic and thermal properties of the β-phase which has hexagonal symmetry.

3.4. N–T_q relations analysed by an Arrhenius-type equation

The thermal-shock crack patterns may be regarded as the two processes of the nucleation and subsequent growth of cracks. Machlin and Nowick [31] and Yokobori [32] have demonstrated that the rate of crack generation, or the probability of occurrence of fracture per unit time in materials under a tensile stress p, can be characterized by an Arrhenius type of equation, where

$$p = A\exp(-U/RT) \quad (6)$$

where $U = U_0 - \Phi(\sigma)$, U_0 = activation energy, $\Phi(\sigma)$ = an energy term depending on the applied stress σ, R = gas constant, T = absolute temperature and A = constant.

Studies of the sub-critical crack growth during thermal fatigue of glasses and ceramics indicate that the crack growth behaviour may also be assumed to be described by exponential equations [33, 34] of the form

$$V = V_0 \exp\left(\frac{-U + bK_I}{RT}\right) \qquad (7)$$

or

$$V = AK_I^n \exp(-Q/RT) \qquad (8)$$

where V = rate of sub-critical crack growth, V_0, A and b = constants, K_I = stress intensity factor, n = stress intensity exponent, U and Q = activation energy. Atkinson [35] has suggested that sub-critical crack growth behaviour in geological materials including quartz can be described by Equation 8, for Equation 7 can only be used to describe the stress corrosion portion of the "stress intensity factor–crack velocity diagram" (K_I–V diagram). In contrast, Equation 8 can often be used to describe the complete K_I–V diagram.

However, crack growth under the thermal stress induced by quenching occurs under the stress condition that $K_I = K_{Ic} \simeq 1$ MPa m$^{1/2}$ in which the crack growth may be governed by Equation 8 under the condition $K_I = K_{Ic}$. The order of crack size, a, nucleated by quenching ($\Delta T \simeq 500\,°C$) corresponding to the condition $K_I = K_{Ic}$ is estimated to be about 4 μm by applying Equation 3 and the well-known relationship

$$K_I = Y\sigma_{th}a^{1/2} \qquad Y \simeq 1 \qquad (9)$$

By considering the quenching process as achieving the stress condition that $K_I = K_{IC}$, it is possible to assume that the cracks which are nucleated at the temperature T_q grow as "macroscopic" cracks during quenching from regions II and III. Therefore, the observed crack densities is assumed to be governed by the rate of crack nucleation which can be characterized by Equation 6. The observed crack densities, N in regions II and III in Fig. 1 may be expressed as

$$N(\mathrm{cm}^{-1}) = A\exp[-U/RT_q(\mathrm{K})] \qquad (10)$$

If the term $\Phi(\sigma)$ is expressed by the relation

$$\Phi(\sigma) = \Phi_0 T_q(\mathrm{K}) \qquad (11)$$

as a function of the quenching temperature, then Equation 10 can be modified to

$$N(\mathrm{cm}^{-1}) = A_0\exp[-U_0/RT_q(\mathrm{K})] \qquad (12)$$

where $A_0 = A\exp[\Phi_0/R]$.

The activation parameters characteristic of the crack densities N_{II} and N_{III} as thermally activated nucleation processes are

Region II: $A_0 = 2.3 \times 10^2(\mathrm{cm}^{-1})$,
$U_0 = 14$ kJ mol^{-1}
Region III: $A_0 = 1.4 \times 10^4(\mathrm{cm}^{-1})$,
$U_0 = 39$ kJ mol^{-1}

Here, the U_0 values may be interpreted as the activation energies associated with the crack nucleation process during thermal shock quenching. Atkinson [35] has reported that the activation enthalpy associated with sub-critical growth of specific crack configurations in synthetic quartz crystals ranges from 54 to 100 kJ mol^{-1} for different environmental conditions between 20 and 250 °C. It has also been reported [36] for several kinds of silicate glass that the activation energies associated with slow crack growth are in the range from 109 to 138 kJ mol^{-1} between 2 and 90 °C. Therefore, it must be concluded that the above activation energies which govern the crack nucleation processes during quenching (T_q = 200–800 °C) of quartz lascas are much smaller than those associated with crack growth processes.

4. Summary and conclusions

The crack patterns created by quenching quartz lascas as the pre-treatment for ball milling can be classified into three types based on the quenching temperature. These are: below ~200 °C (region I), from ~200 °C to T_c (573 °C) (region II), above T_c (region III). Region I is regarded as that region where cracks pre-existing on the lasca surface grow or extend under the influence of the thermal stresses induced by the critical temperature differential, estimated to be about 70 °C. In regions II and III, new cracks appear to be nucleated on the lasca surface by the thermal stresses. Crack densities measured as a function of the quenching temperatures in regions II and III are well described by an Arrhenius equation. Activation energies were evaluated to be 14 and 39 kJ mol^{-1} in regions II and III, respectively. They are interpreted as the activation energies associated with the crack nucleation processes in two regions, one below T_c and one above.

The individual grains which were obtained after quenching exhibit two distinct geometries, depending on T_q. A granular shape is obtained for region II ($T_q < T_c$) and a needle-like shape in region III ($T_q > T_c$). These differences of shape are believed to be the consequence of differences of crack generation pattern which are governed by the elastic and thermal properties in the α-phase and β-phase of quartz during the quenching process. However, the complete process of crack pattern generation for each temperature region is not yet fully understood.

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