

Hysteresis upon Repeated Cycling through the Beta-Alpha Cristobalite Transformation

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Abstract

Beta-to-alpha transformation in cristobalite was examined by means of differential scanning calorimetry (DSC) to address how enthalpy, transformation hysteresis, and transformation onset temperature change upon repeated thermal cycling. Cristobalite powder was repeatedly cycled from 190–280 °C and back, cycling through the first-order displacive transformation between high-temperature, cubic beta-cristobalite and low-temperature, tetragonal alpha-cristobalite. The enthalpy of the transformation did not change with cycling, but the exothermic beta-to-alpha enthalpy at 1560 ± 27 J/mol was larger than endothermic alpha-to-beta enthalpy at 1260 ± 8 J/mol. Transformation onset temperatures and hysteresis varied systematically with repeated cycling of the transformation. The onset temperature of the beta-to-alpha transformation increased logarithmically with cycling, resulting in reduced under-cooling and hysteresis. The onset temperature of the alpha-to-beta transformation decreased logarithmically with cycling, resulting in reduced super-heating and hysteresis. The reduced hysteresis indicates a lowered barrier to transformation. We propose this reduced hysteresis indicates particle refinement through microfracture caused by the -4.9 % volume change on the beta-to-alpha transformation. This is supported by the observation of powder size dependence. Powder with particles finer than 38 μm had no change on cycling, suggesting 38 μm is below the critical minimum size.

Keywords: Cristobalite, silica, phase transformation, hysteresis

I. Introduction

Like other silicate crystal structures, cristobalite exhibits a higher symmetry form at high temperature and undergoes a transformation to a lower symmetry form at low temperature¹. In cristobalite the high-temperature, cubic beta-cristobalite structure is the stable structure for silica from 1470 to 1625 °C, but persists meta-stably to lower temperatures. It undergoes a first order, displacive transformation to tetragonal alpha-cristobalite between 275 and 200 °C^{2, 3, 4, 6, 7}. The transformation temperature is highly variable and dependent on the thermal history of material as noted by Wyckoff in 1925² and Hill and Roy in 1958⁵. The exact nature of the transformation and the precise structure of beta-cristobalite itself remains an active area of research. The cubic structure of beta-cristobalite was first reported by Wyckoff² in 1925, but in 1937 Nieuwenkamp³ proposed the structure is actually dynamically disordered at a local level. As observed by several authors, notably, Wright and Leadbetter in 1975⁸, the ideal cubic structure results in bond angles and lengths atypical for SiO₂. This topic has been examined with a range of experimental techniques, including TEM by Withers *et al.*^{9, 10}, NMR by Spearing *et al.*¹¹, neutron diffraction by Dove *et al.*¹², and Raman spectroscopy by Swainson *et al.*¹³. The transformation has been treated by Schmahl *et al.*¹⁴ using a Landau free energy approach,

while Swainson and Dove¹⁵ and Huang *et al.*^{16, 17} used MD simulation, and Cope and Dove¹⁸ used a Pair Distribution Function Approach. The general conclusion is drawn that beta-cristobalite, while retaining cubic symmetry, is dynamically disordered, but the details continue to be actively researched.

The transformation from beta-to-alpha is accompanied by a 4.9 % volume reduction⁶, leading to a dependence on stress. The effect of hydrostatic pressure was studied by Cohen and Klement in 1975¹⁹, and other aspects of the role of the stress state on the transformation were explored by Parise *et al.* in 1994²⁰, Lee and Lee in 2001²¹, and Chao and Lu in 2002²². The origin of this hysteresis was discussed in detail by Schmahl in 1993^{23, 24}.

In this paper we are interested in the role of thermal history on the hysteresis for this transformation. In particular, we investigate how repeated cycling changes the hysteresis of the transformation from alpha-cristobalite to beta-cristobalite on heating, and the reverse transformation from beta-cristobalite to alpha-cristobalite on cooling. We will report that the transformation temperature of the alpha-to-beta endotherm upon heating and beta-to-alpha exotherm on cooling changes systematically with repeated cycling. The transformation enthalpy does not change with repeated cycling, although the beta-to-alpha exotherm is consistently larger than the alpha-to-beta endotherm. We will present evidence that this is related to

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dissipation of stresses associated with the volume change of the transformation.

II. Procedure

(1) Materials

We used a commercial amorphous silica powder (TECO-Sphere-Microdust, CE Minerals, Greenville, TN), which is 99.7 % silica with primary contaminants of alumina and iron oxide. The powder is spheroidized in a drop-melt process, resulting in a distribution of 5–25- μm particles of roughly spherical shape. Details of the powder characteristics were previously reported²⁵.

Phase-pure cristobalite was produced according to the procedure of Wang and Hon²⁶. The powder was annealed under lab air at 1550 °C for 24 h followed by grinding, annealed at 1550 °C for 12 h followed by grinding, and annealed again for 12 h. Thus the material for our first cycle of heating in the DSC had been heated and cooled three times, and had experienced three beta-to-alpha transformations before DSC and one transformation since last annealing at 1550 °C. Size fractions were produced by means of sieving the powder to collect fractions with the following particle size ranges: coarser than 425 μm , 150–425 μm , 106–150 μm , 38–106 μm , and finer than 38 μm .

(2) Calorimetry

Calorimetry was conducted on a TA Q2000 Differential Scanning Calorimeter (TA Instruments-Waters LLC, New Castle, USA), calibrated with the melting point of indium and heat capacity of sapphire. Transformation enthalpies were obtained with the TA Platinum™ DSC software. A sample of powder was sealed in a Tzero™ aluminum hermetic DSC pan and a hole was punctured to allow the escape of gas. Nitrogen was used as a cover gas. Testing was conducted based on cycling of the material from 190 °C to 280 °C with heating/cooling rates of 3 °C/min, for up to 50 cycles. The onset temperature for the alpha-to-beta exotherm is defined as the temperature where the heat flow reached 25 % of the exothermic peak of that cycle. The onset temperature for the alpha-to-beta endotherm is defined as the temperature where the heat flow reached 25 % of the endothermic peak of that cycle. Note that the DSC calorimetry was for alpha-cristobalite prepared by multiple heating, so it had already been transformed from beta-to-alpha during cooling from its 1550 °C crystallization temperature. What we call “Cycle 1” is the first heating cycle we recorded in the calorimeter.

III. Results

(1) Influence of repeated cycles on the beta-alpha transformation

The DSC curves for Cycle 1 and Cycle 50 can be seen in Fig. 1. On heating from 190 °C to 280 °C an endothermic peak corresponding to the alpha-to-beta transformation can be observed at 259–261 °C, while on cooling an exothermic peak corresponding to the beta-to-alpha transformation is observed at 235–239 °C. The

DSC curves for Cycle 1 and Cycle 50 are compared in Fig. 1.

For Cycle 1, the onset temperature for the endothermic alpha-to-beta transformation during heating occurred at 259.4 °C and the endotherm was complete at around 263 °C. The onset temperature for the exothermic beta-to-alpha transformation on cooling occurred at 236.8 °C and was complete at around 234 °C. There was a 22.6 °C hysteresis for the onset temperatures for the exotherm and endotherm for Cycle 1. For Cycle 50, the alpha-to-beta endotherm upon heating had an onset temperature of 259 °C, the beta-to-alpha exotherm onset upon cooling occurred at 238.7 °C. The hysteresis at Cycle 50 was 20.3 °C, which was smaller than the onset hysteresis for Cycle 1. The width of the thermal events, from onset to finish, is broader by about 40 % after Cycle 50, indicating an increased range of phase coexistence. The onset of the alpha-to-beta endotherm decreased by 0.4 °C after 50 cycles, while the onset of the beta-to-alpha exotherm increased 1.9 °C after 50 cycles.

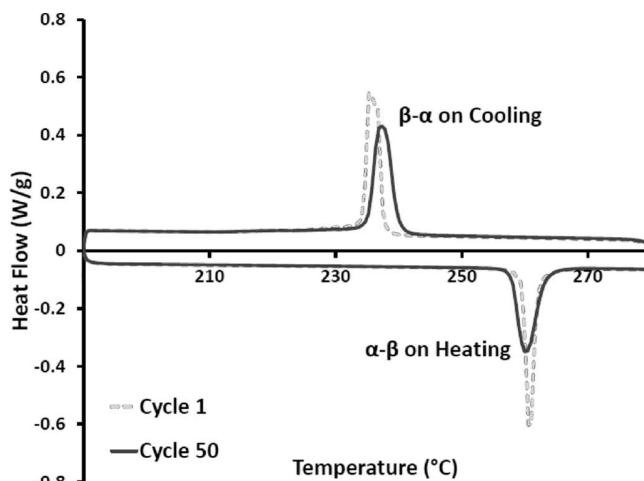


Fig. 1: DSC curves for Cycle 1 and Cycle 50. Material was previously cooled once from beta to alpha prior to testing.

Details of the endothermic and exothermic events for ten selected cycles appear in Fig. 2, which compares the endotherm for alpha-to-beta (Fig. 2a) and the exotherm for beta-to-alpha (Fig. 2b) for the first three cycles 1, 2, 3 with cycles 10, 20, 30, 40, and with the last three cycles 48, 49, and 50. The cooling beta-to-alpha exotherms broaden and move to incrementally lower temperatures, while the heating alpha-to-beta endotherms broaden more and have a larger temperature increment.

The transformation enthalpy, determined by integration of the thermal events with the DSC software, does not change with cycling. Fig. 3 displays the enthalpies as J/g, and it is apparent that there is no change. The enthalpy for the beta-to-alpha exotherm was 1560 ± 27 J/mol while the enthalpy for alpha-to-beta endotherm was 1260 ± 8 J/mol. Note the substantial difference between the exotherm and the endotherm, which is about 300 J/mol or about 20 %. This large difference indicates a significant dissipation of energy during the transformation of beta-cristobalite to alpha-cristobalite.

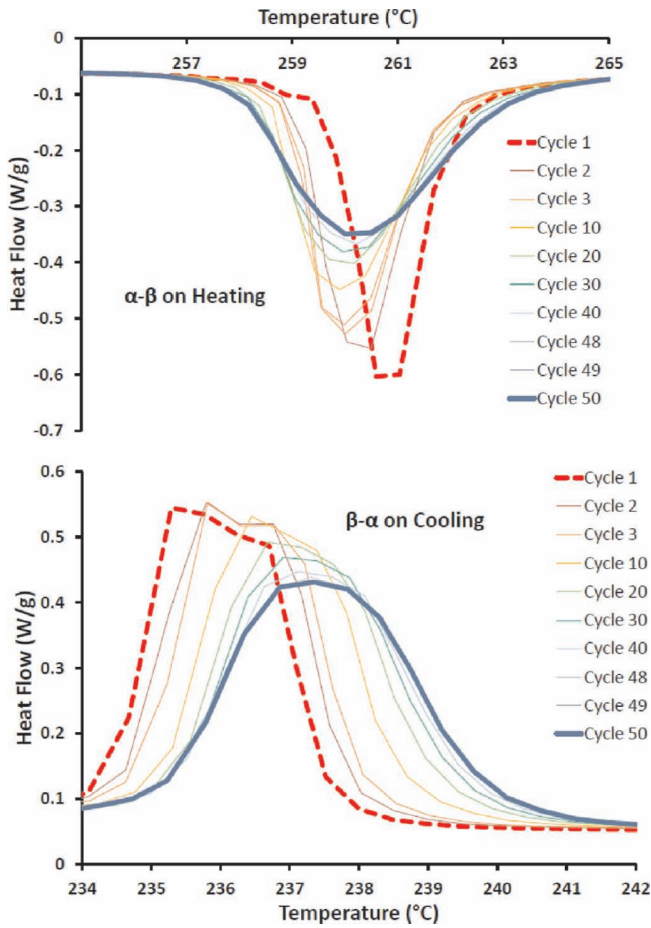


Fig. 2: Observed exotherm from beta-to-alpha transition on cooling and endotherm from alpha-to-beta transition on heating through repeated cycling. The peaks are seen to shift monotonically with the onset temperature of the endotherm decreasing with each cycle and the onset temperature of the exotherm increasing with each cycle. (A) Endotherm corresponding to alpha-to-beta transition (B) Exotherm corresponding to beta-to-alpha transition.

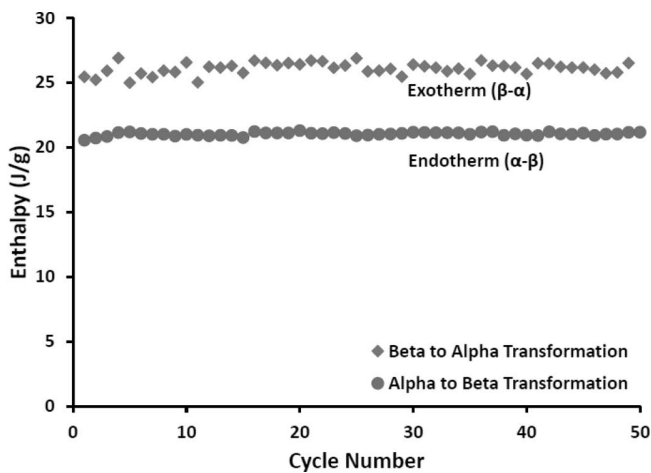


Fig. 3: Transformation enthalpy as found by integration of peak area.

The onset temperature of the exotherm corresponding to the beta-to-alpha transformation increased systematically with the number of cycles. This increase of temperature of the exotherm onset corresponds to a decrease in the undercooling of the transformation. The temperature of onset is plotted in Fig. 4. The onset temperature in-

creases monotonically, and can be fit to the following relation:

$$T_{\text{onset}}^{\beta-\alpha} = 236.8 + 0.473 \ln(n) \text{ } ^\circ\text{C} \quad (1)$$

in which n is the cycle number. This implies there is an incremental increase in the temperature of transformation to alpha which diminishes with the number of cycles with a logarithmic decrement of $\gamma_{\beta \rightarrow \alpha} = +0.473^\circ$, or

$$\frac{\delta T_{\text{onset}}^{\beta-\alpha}}{\delta \ln(n)} = \gamma_{\beta \rightarrow \alpha} = +0.473 \text{ } ^\circ\text{C} \quad (2)$$

This corresponds to less hysteresis and reduced supercooling required to transform, implying a lower driving force necessary for the transformation with each passing cycle.

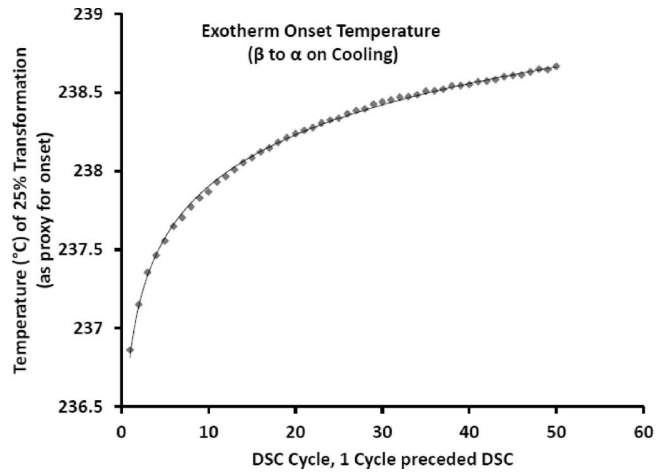


Fig. 4: Beta-to-Alpha onset temperature as a function of cycle number of the beta-to-alpha exotherm. The line is a fit with Equation 1.

The onset temperature of the endotherm corresponding to the alpha-to-beta transformation was established with the same method as the exotherm and is plotted in Fig. 5. The onset temperature increases with each cycle for the first 20 cycles, afterwards it remains constant at $258.9 \pm 0.03 \text{ } ^\circ\text{C}$. This corresponds to a decrease in super heating. The onset temperature could be fit to a logarithmic function through 20 cycles, as:

$$T_{\text{onset}}^{\alpha-\beta} = 259.5 - 0.183 \ln(n) \text{ } ^\circ\text{C} \quad (3)$$

in which n is the cycle number. This implies there is an incremental decrease in the temperature of transformation to beta-cristobalite which diminishes with the number of cycles with a logarithmic decrement of:

$$\frac{\delta T_{\text{onset}}^{\alpha-\beta}}{\delta \ln(n)} = \gamma_{\alpha \rightarrow \beta} = -0.183 \text{ } ^\circ\text{C} \quad (4)$$

Thus the alpha-to-beta transformation exhibits a logarithmic decrease in the driving force necessary for the transformation with each passing cycle until stabilizing after 20 cycles.

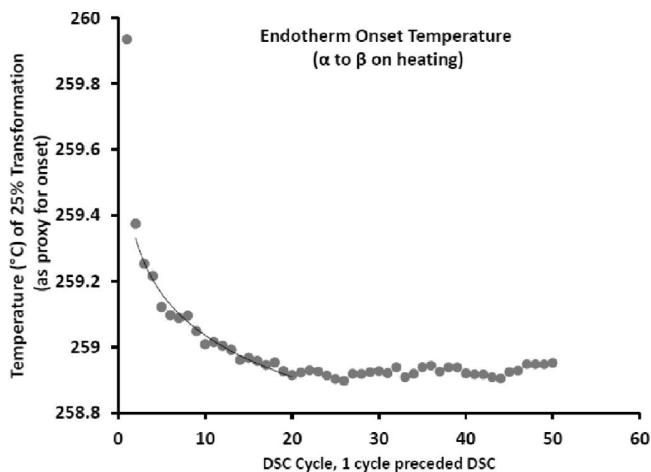


Fig. 5: Alpha-to-beta onset temperature as a function of cycle number of the alpha-to-beta endotherm. The line is a fit of the first 20 cycles with Equation 3.

(2) Influence of particle size on behavior with repeated cycles

It is known that in order to accommodate the strain of the beta-to-alpha transformation the material undergoes extensive microfracture and twinning. It has previously been reported that cristobalite twinning displays no memory on repeated transformation⁹. To examine the influence of particle size, the powder was sieved into the following size fractions: 150–425 μm , 106–150 μm , 38–106 μm , and finer than 38 μm . Samples from each fraction were cycled for 50 cycles. The DSC curves for Cycles 1 and 50 for the finer than 38- μm fraction and the 150–425- μm fraction can be seen in Fig. 6. The fraction finer than 38 μm has no change in hysteresis over 50 cycles, while the coarser fraction has a noticeable change in hysteresis after 50 cycles. The change in the beta-to-alpha onset for sieved fractions and the whole powder are reported in Fig. 7. For the larger particle fractions, the onset temperature increased, so the under-cooling decreased on cycling. It can be observed that the coarser 150–425- μm particles display less change in enthalpy with cycling than the smaller 150–38 μm powder. The whole powder containing the entire distribution of sizes displays an averaged behavior between that observed for the large particle and small particle distributions. Particles smaller than 38 μm do not show a cycling effect, while those with sizes 38–106 μm do. This suggests that a d_{crit} exists and falls between 106 and 38 μm . The middle course size fractions, 150–106 μm and 106–38 μm , actually have a larger logarithmic increment of 0.72 ± 0.04 than the whole powder.

IV. Discussion

(1) Hysteresis of the beta-alpha transformation and changes upon cycling

The hysteresis in the transformation between the beta and alpha phases of cristobalite is related to the volume change associated with the transformation. There is a significant strain energy associated with the initial nucleation of the new phase in the host phase during both the beta-to-alpha and alpha-to-beta transformations. Overcoming this strain energy requires an associated driving

force, which manifests as a transformation hysteresis. In addition to the localized strain at the beta-alpha boundary, macroscopic strain fields can develop owing to the transformation volume change. As reported by others, the phase transformation is responsive to the macroscopic stress state and particle size of the material^{19,20,22,25,27}. We believe the change in hysteresis on cycling is the alleviation of some of this macroscopic stress by microfracture. Microfracture can reduce overall constraint on the transformation and lower the barrier to transformation. However, microfracture can only occur so long as the strain energy relieved by the fracture exceeds the energy required for fracture to occur. Eventually, microfracture induced by cycling through the beta-alpha transformation will reduce the particle size below the critical size necessary to drive further microfracture, and further cycling will have no effect.

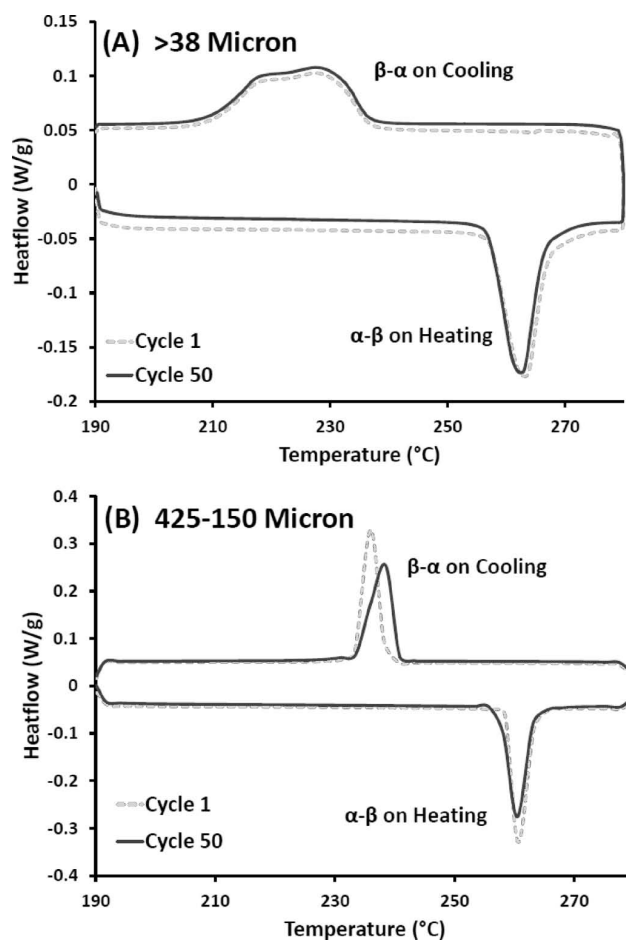


Fig. 6: DSC curves for Cycle 1 and Cycle 50 for sieved powder fractions. (A) Particles finer than 38 μm (B) Particles in the size range 425–150 μm .

The change in transformation temperature with cycling is greater for the beta-to-alpha transformation than the alpha-to-beta transformation. The beta-to-alpha transformation temperature change per cycle is 0.473 K/n and continues to change at this rate for 50 cycles. The alpha-to-beta transformation temperature change per cycle is -0.183 K/n and stops changing after 20 cycles. This difference may be due to the stress state induced by each transformation. The beta-to-alpha transformation results in a volume reduction and therefore the development of primarily ten-

sile stresses in the material, while the alpha-to-beta transformation results in a volume expansion and therefore the development of primarily compressive stresses in the material. Silica being a brittle material, the failure criterion for silica is far lower under tension than under compression, therefore one might expect more fracture at lower stresses during the beta-to-alpha transformation than during the alpha-to-beta transformation. This may explain the larger changes in the onset temperature of the beta-to-alpha transformation.

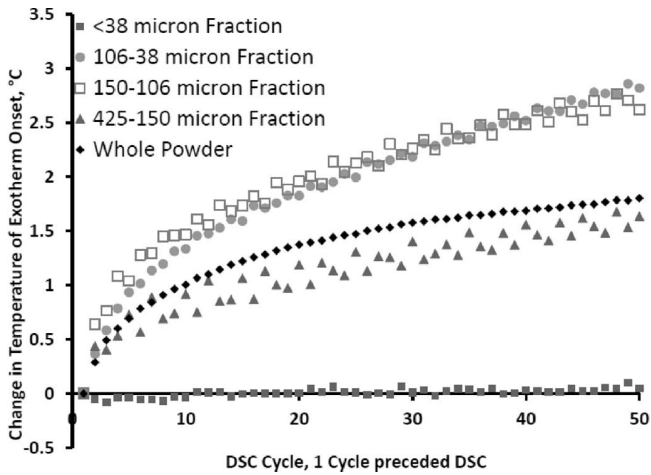


Fig. 7: Change in beta-to-alpha exotherm onset temperature for sieved powder fractions.

The enthalpy of transformation differs between the transformation from beta-to-alpha and from alpha-to-beta, as reported by others^{28,29,30,31}. We found the enthalpy of transformation from beta-to-alpha to be 1560 ± 27 J/mol and the enthalpy of transformation from alpha-to-beta to be 1260 ± 8 J/mol. This falls at the higher end of the range found in the literature of 1100–1430 J/mol for beta-to-alpha transformation and 1020–1280 J/mol for alpha-to-beta transformation^{14,28,32}. The difference in the transformation enthalpies between the forward and reverse transformation indicates there is an irreversible energy loss of ~ 300 J/mol. The difference in enthalpy between the beta-to-alpha and alpha-to-beta transformations was found to be invariant across cycling even as the onset temperatures changed and hysteresis lessened.

Similar behavior has been reported for the metallic Ni-Ti (Nitinol) system, which has a thermoelastic martensitic transformation. Nitinol displays a change in transformation temperature which changes with number of cycles with a constant logarithmic decrement, similar to what we observe in cristobalite^{32,33}. The enthalpy of the transformation in Nitinol differs between the forward and reverse transformation, which is attributed to irreversible energy loss due to friction and dislocation formation and movement^{32,33}. While dislocations activity in the cristobalite is unlikely to play a role, there is extensive twinning which may be producing a similar result.

It should be noted that there is a significant fraction of impurity within the silica tested with a manufacturer’s listed purity of 99.7%. It is known the temperature at which the beta-alpha transition occurs is sensitive to impurities^{1,4,7}. The impact of impurities on the change of beta-alpha transformation enthalpy is unknown but may

be significant. Further study could shed light on the role of impurities based on testing of both higher- and lower-purity material.

(2) Transformation temperature decrement related to stress

The hysteresis in the transformation implies that unrelaxed elastic strain energy could be involved. The beta-to-alpha transformation is associated with a volume contraction suggesting tensile stresses, while the alpha-to-beta transformation is accompanied by a volume dilation suggesting compressive stresses. The cycling effect can be restated in terms of elastic stresses using a Clausius-Clapeyron formulation. Let us consider the hydrostatic elastic stress (σ_h) from the volume change of the transformation to be equivalent to a pressure. From the Clausius-Clapeyron equation, we would expect the pressure-induced change in transformation temperature to be related to the enthalpy and volume change:

$$\frac{dP}{dT} = \frac{d\sigma_h}{dT} = \frac{\Delta H}{T\Delta V} \tag{5}$$

Using the average transformation temperature (248 °C or 521 K), a value of 1560 J/mol for the enthalpy, and a volume change of 4.9% of the beta-cristobalite molar volume (2.57×10^{-5} m³/mol), the magnitude of $\Delta H/T\Delta V$ is about 2.4 MPa/K. We observe how the transformation temperature changes with repeated cycles, $dT/dn = \gamma/n$, and can infer how the unrelaxed transformation stress changes with repeated cycles, $d\sigma_h/dn$. Using the Clausius-Clapeyron and a chain rule analysis we can relate the transformation temperature change per cycle to the change in the unrelaxed stress per cycle:

$$\frac{dT}{dn} = \frac{\gamma}{n} = \frac{dT}{d\sigma_h} \frac{d\sigma_h}{dn} = \frac{T\Delta V}{\Delta H} \frac{d\sigma_h}{dn} \tag{6}$$

where γ/n is the empirical dependence of transformation temperature changing with the cycle number.

$$\frac{d\sigma_h}{dn} = \frac{\Delta H}{T\Delta V} \frac{\gamma}{n} \tag{7}$$

or expressed as the logarithmic increment of the elastic stress:

$$\frac{d\sigma_h}{d\ln(n)} = \left(\frac{\Delta H}{T\Delta V} \right) \gamma \tag{8}$$

Using the observed value of the logarithmic increment for the beta-to-alpha transformation, +0.473 °C/cycle, this implies the logarithmic increment of unrelaxed elastic stress is $d\sigma_h/d\ln(n) = +1.14$ MPa. For the reverse transformation from alpha-to-beta on heating, the logarithmic increment of unrelaxed elastic stress is $d\sigma_h/d\ln(n) = -0.44$ MPa. The stress increment alpha-to-beta transformation is smaller in magnitude and opposite in sign, suggesting that the dilation upon transforming back to beta-cristobalite can relax less effectively than the reverse transformation to alpha-cristobalite. The transformation on cooling from beta-to-alpha is associated with a volume reduction and the development of a tensile strain. This tensile strain can be partially relieved by microfracture. Conversely, the alpha-to-beta transformation on heating is associated with a volume expansion and alleviation of

the prior twinning. Some fraction of this expansion will be accommodated by the closing of the cracks formed on the beta-to-alpha transformation, some may be balanced by retained tensile stress, and the remainder will develop as a compressive stress. At the low temperatures used in this study no relaxation of stress by thermal annealing was possible. The smaller hysteresis is the result of continued microfracture reducing the macroscopic constraints on the volume change associated with the transformation. Fracture reduces volumetric constraint from surrounding material, lessening the stress or internal pressure associated with transformation. Thus continued microfracture on each cycle could reduce the stored strain energy associated with transformation and reduce the driving force needed to transform.

Twinning could also play a role, as the loss of symmetry from cubic to tetragonal with transformation from beta-to-alpha leads to extensive twinning in the alpha-cristobalite^{11, 15, 35}. The excess energy associated with twins can contribute to the hysteresis. The twin microstructures do not show memory on repeated transformation¹⁰, suggesting that “training” upon repeated transformation might not cause a systematic change in the hysteresis on cycling. Evaluating this would require information on twin structures, particularly how they might change with cycling. The calorimetric data in this paper cannot address this issue.

The continued microfracture mechanism is consistent with the results from the powder fractions of varying size, where it was observed that no cycling effect occurred when the particle size was small. If the cycling effect was caused by a microstructural phenomenon such as the training of the material by repeated twinning there is no reason for the effect to be absent in particles of 38 μm in size. However, if the cycling effect is due to continued microfracture, one does expect that for a certain size cracking will no longer occur and no effect from cycling will be seen. The lack of any impact of cycling on hysteresis for powder with 38 μm or finer particles suggests this size falls below the critical size necessary for microfracture.

(3) Comparison to thermoelastic martensitic transformations

Certain aspects of the cristobalite transformation are similar to martensitic transformations²³. The well-studied displacive thermoelastic martensitic transformation in NiTi (Nitinol) can be compared to the beta-alpha transformation in cristobalite. The beta-alpha transformation in cristobalite is not a martensitic transformation; however, as displacive transformations displaying hysteresis, there are parallels. The impact of cycling NiTi through the martensitic phase transformation was reported on by McCormick and Liu in 1994³² and Pelton *et al.* in 2012³³. They found the onset temperature of the transformation on heating and on cooling both decreased logarithmically with the hysteresis between onset temperatures remaining constant. The transformation enthalpy was also found to decrease. This contrasts with our observations in cristobalite in which the hysteresis decreases but the transformation enthalpy remained constant. McCormick and Liu explain cycling phenomena using the methods of

Salzbrenner and Cohen³⁵, which can in turn be applied to the cristobalite transformation to test the applicability of established martensitic theory to the cristobalite transformation.

The Salzbrenner-Cohen theory posits the transformation free energy of the martensitic transformation can be broken into three components: chemical free energy, ΔG_c ; stored (recoverable) elastic strain energy, ΔE_e ; and irreversible energy loss due to friction and moving of interfaces, ΔE_i . Since, ΔG_c doesn't change, the transformation temperature can be reported by:^{32, 35}

$$T^{H-L} = T_o + \frac{(\Delta E_c^{H-L} + \Delta E_i^{H-L})}{\Delta S^{H-L}} \quad (9)$$

in which T_o is the equilibrium transformation temperature and the superscript H-L indicates transformation from the High- to Low-temperature phase corresponding to the parent-to-martensite transformation in NiTi or the beta-to-alpha transformation in cristobalite. The reverse transformation would be indicated by an L-H superscript. The equilibrium temperature can be defined by $T_o = \Delta H/\Delta S$. McCormick and Liu in applying the Salzbrenner-Cohen theory state the irreversible energy loss term can be found from:³²

$$\Delta E_i = \frac{(T_{H \rightarrow L} - T_{L \rightarrow H})\Delta S}{2} \quad (10)$$

Using the available data on the cristobalite beta-alpha transformation we can calculate this ΔE_i and compare it to the observed irrecoverable energy loss, thereby evaluating the applicability of established martensite theory for the beta-alpha transformation of cristobalite. The equilibrium transformation temperature is calculated with:

$$T_o = T_{\text{peak}}^{H-L} + \frac{T_{\text{peak}}^{H-L} - T_{\text{peak}}^{L-H}}{2} \quad (11)$$

which yields $T_o = 248.2^\circ\text{C} = 521.4 \text{ K}$, from which $\Delta S = 3.0 \pm 0.05 \text{ J/mol}\cdot\text{K}$ is obtained based on the enthalpy of 1560 J/mol. Using Eq. 10, this yields a ΔE_i of $69 \pm 1 \text{ J/mol}$ which is a small fraction of the observed irrecoverable energy loss of 300 J/mol as observed from the difference between the enthalpy of the forward and reverse transformation. The Salzbrenner-Cohen theory for hysteresis of martensitic transformations underestimates the hysteresis of the beta-alpha transformation in cristobalite. Perhaps this is because the cristobalite transformation is not a thermoelastic martensitic transformation. The changes caused by cycling in the NiTi system have been attributed to dislocation accumulation, and this mechanism is not likely to play a role in cristobalite. Despite both being displacive transformations exhibiting hysteresis, the reported behavior in NiTi differs from that we observe in cristobalite and the difference in structure and deformation in the metallic NiTi and the brittle, covalent cristobalite limit comparisons.

V. Conclusions

Repeated cycling of sintered cristobalite powder was observed to display a decrease in the endotherm onset temperature and an increase in the exotherm onset temperature, reducing the transformation hysteresis. The temperature of the beta-to-alpha transformation was found to

follow $T_{\text{onset}}^{\beta-\alpha} = 236.8 + 0.473 \ln(n) ^\circ\text{C}$, while the temperature of the alpha-to-beta transformation was found to follow $T_{\text{onset}}^{\alpha-\beta} = 259.5 - 0.183 \ln(n) ^\circ\text{C}$. The logarithmic decrement suggests a change in the transformation strain energy follows $\sim 1/n$. This decrease in the required super heating and cooling respectively indicates a lower energy barrier to transformation. It was found that for powders below a critical particle size between 106 and 38 μm no cycling effect occurred. This suggests the possibility that the cycling effect is caused by continued microfracture which cannot occur below a critical particle size.

The enthalpy of transformation was found to be 600 J/g greater for the beta-to-alpha than for the alpha-to-beta transformation. The enthalpy did not change on cycling even as transformation hysteresis was reduced.

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