

Quenching of solid samples for high temperature equilibrium measurement

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The quenching rate required to "freeze-in" high temperature states depends on the resolution attained in the observational technique used and on the kinetics of the property changes that may occur in the sample. For a successful quench, heat must be removed before observable changes occur. Heat loss during travel to the quench bath must be minimized as this lowers the certainty of the quenched-in temperature state, while the heat removal rate after immersion in the quench bath should be maximized. The required quench rate will determine the necessary sample size and quench medium. Quenching has been experimentally evaluated for a propelled "insulating envelope" sample transfer quench device. Results are used to determine optimum conditions for effective quenching. A procedure is established to guide the choice of sample size and quench medium to attain an adequate quenching rate.

1. Introduction

In many materials systems it is difficult to make *in situ* measurements of actual equilibrium states at high temperatures. These systems are usually studied by quenching equilibrated samples and then examining the structures at room temperature. The classical procedure for silicate systems was developed at the Geophysical Laboratory [1]. As Levin *et al.* describe it [2], a sample is rapidly quenched by "dropping it instantaneously into a liquid at low temperature". In fact, the drop time is normally a few tenths of a second, during which changes in the sample may conceivably happen. Both changes during sample transfer and the cooling rate in the quench medium must be considered in evaluating the quench process.

In this paper we first analyse the two-step process used for quenching solids. After a brief review of the rate-limiting steps for heat removal, an improved quenching device is described and the physical parameters of this device and several different quench media are evaluated. Finally, these data are used to develop a procedure for optimizing quenching in any system of interest. The optimization process is described using precipitation of magnesioferrite from iron-saturated magnesium oxide as an example.

2. Normal quenching

Normal quenching is a two step process. First, the equilibrated sample travels from the furnace to the quench bath. Rapid heat removal in the quench bath freezes in the high temperature state. Each of these regimes involves cooling, but the travel regime normally has a lower heat transfer coefficient and, therefore, a smaller rate of cooling. Heat transfer during travel is the sum of the radiated heat and that conducted to the travel environment. Heat transfer during quenching includes the same radiative component, but a higher conductive heat transfer coefficient. Two characteristics of the overall process are important. First, the cooling rate on immersion must be fast enough to ensure that no observable property variation has occurred. Second, little or no cooling should occur during travel, since this would change the state of equilibration.

For liquids, splat cooling of a relatively large drop allows a low surface-to-volume ratio for the travel step, preventing large amounts of heat loss. Splattering creates a geometry with a large surface-to-volume ratio, which causes rapid cooling during the quench. By imposing dimensional changes on the liquid, one can easily optimize the two-step quench process. In other processes, such as laser

melting of a thin surface layer, the travel step may be very nearly "instantaneous". Yager and Kingery [3] used samples heated by laser radiation; quenching was done by pouring liquid nitrogen on to them synchronized with the laser shut-off, providing near instantaneous quench "travel". Similar methods have used wire or foil which is self-heated and then quenched by the application of the quench medium [4, 5].

The rate of heat removal may be limiting by conduction in the sample itself, or by the heat transfer coefficient to the quench medium. When the cooling environment is rate limiting (Newtonian cooling), there are no thermal gradients in the sample. Under these conditions the initial cooling rate for a wafer cooled from both sides in the quench bath ([6], p. 292) is:

$$\dot{T} = \frac{h^a(T_f - T_q)}{\rho C_p L} \quad (1)$$

and the temperature change during the transfer from furnace to quench is:

$$\Delta T^{tr} = \frac{h^{tr}(T_f - T_{tr})t}{\rho C_p L} \quad (2)$$

where $T_f - T_q$ is the temperature difference between furnace and quench bath, $T_f - T_{tr}$ is the temperature difference between furnace and transfer environment, h is the heat transfer coefficient of the quench bath or the transfer environment respectively, ρ is the density, C_p is specific heat capacity, t is the time of travel from the hot zone to the quench surface, and L is half the sample thickness.

When heat conduction in the solid is rate limiting, the cooling rate in the quench bath can be approximated* as:

$$\dot{T} = \frac{k(T_f - T_q)}{\rho C_p L^2} \quad (3)$$

and the temperature change during sample transfer as:

$$\Delta T^{tr} = \frac{k(T_f - T_{tr})t}{\rho C_p L^2} \quad (4)$$

with k being the sample thermal conductivity.

No matter which cooling regime is dictated by sample properties and quench bath heat transfer coefficient, decreasing the sample thickness gives a much more rapid quench rate. However,

*This equation is obtained by expanding the time derivative of temperature into dimensionless form and substituting the appropriate values: $dT/dt = (dT/d\theta) (dF_0/dt) (d\theta/dF_0)$, where θ is dimensionless temperature and F_0 is dimensionless time (see [6], p. 297). When heat transfer in the sample is the limiting step ($B_1 > 10$), $d\theta/dF_0 \approx 1$ (see [6], p. 310) over the range where most of the cooling occurs.

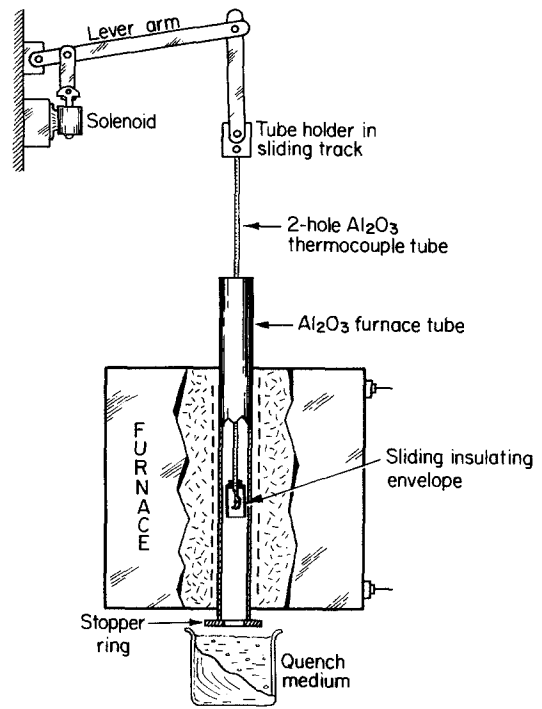


Figure 1 Overall view of propelled insulating envelope (see Fig. 2) that minimizes cooling during sample transfer from the heat treating furnace to the quench bath.

decreasing L also increases the temperature change during sample transfer from the furnace to the quench bath. For a given sample size and temperature level, this temperature change can only be decreased by decreasing the transfer time.

3. Experimental techniques

A device similar to one described by Lengeler [7] was built to minimize the temperature change during sample transfer from furnace to quench bath. A small section of insulating material surrounds the sample during equilibration. This envelope moves with the sample to a point just above the cooling bath surface (Fig. 1). Thus, exposure of the sample to a cooling environment during travel is prevented, the effective time of travel is lowered, and less heat is lost before entry into the quench medium. Fig. 2 illustrates the travelling insulating envelope. A solenoid driven lever propels the sample and envelope from the hot zone at an increased velocity. This also decreases the travel time and heat loss.

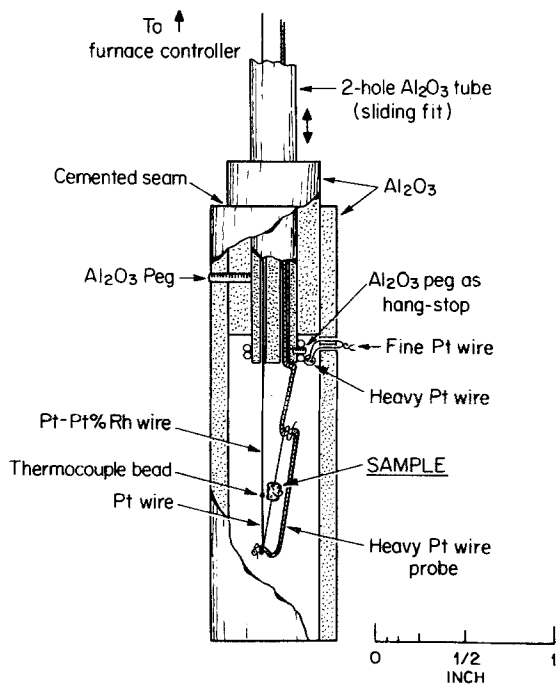


Figure 2 Detail of the insulating envelope that is propelled with the sample from the heat treating furnace to a stop just above the quench bath. Holding the sample as shown has been found suitable for thin ($\sim 100 \mu\text{m}$) ceramic slabs.

To measure the heat transfer coefficient during sample travel and during quenching, a microthermocouple was quenched and its output monitored on an oscilloscope. Different transfer modes were examined, and different quench media characterized; heat transfer coefficients were calculated from the rate of temperature change during Newtonian cooling (Equation 1). Tables I and II show the heat transfer coefficients found for different sample transfer methods and for different quench media. Heat transfer coefficients measuring the values during sample transfer are in accord with values expected for radiative cooling at the temperatures of measurement

TABLE I Heat transfer coefficients during sample transfer from furnace at 1100°C

	Duration (sec)	$h(\text{cal cm}^{-1} \text{cm}^{-1} \text{sec}^{-1} \text{K}^{-1})$
Drop transfer	0.165	0.0019
Propelled transfer	0.085	0.0023
Drop transfer with Insulating envelope		
Travel in envelope	0.144	none
Transfer	0.021	0.0018
Propelled transfer with Insulating envelope		
Travel in envelope	0.075	none
Transfer	0.010	0.0022

(about 1100°C). Quench media results are in agreement with data in the literature ([6], p. 259, [8]).

4. Quench optimization

The basic problem in choosing an optimum sample size and quench is that a small sample size which increases the quench rate also increases the temperature change during sample transfer. Major factors which must be considered in obtaining an optimal quenching process are the observational technique used (its spatial resolution) and the kinetics of change during cooling. These will determine the sample size. In turn, the sample size will dictate quenching furnace design requirements, if it is necessary to lower the temperature change during sample travel. A step-by-step procedure to arrive at an optimal process is described in Fig. 3.

To illustrate the procedure, we shall consider quenching magnesium oxide containing iron oxide in solid solution. Since the solubility of iron in the MgO lattice decreases as the temperature is lowered, magnesioferrite precipitates may form on cooling. These precipitates nucleate at grain boundaries in a polycrystalline matrix ([9], p. 440). The rate-limiting step for the growth of these particles is diffusion of the dissolved iron from the grains to the grain-boundary precipitates.

Step one is to determine the observational resolution of the experimental technique that will be used to study the quenched material. For comparison, optical microscopy and electron microscopy will be considered. For optical microscopy the resolution is about $0.5 \mu\text{m}$; for electron microscopy the resolution selected is that for chemical profiling in the scanning microscope, about 10 nm. Our criteria is that no visible changes occur; for better observational resolution, a higher quenching rate would be required.

TABLE II Measured heat transfer coefficients of different media

Quench medium	Temp. (K)	h (cal cm ⁻¹ cm ⁻¹ sec ⁻¹ K ⁻¹)
Air	298	0.0033
Liquid nitrogen	77	0.011
Water	298	0.072
Oil	298	0.080
Liquid tin	850	0.50

Step two is to estimate the rate at which observational changes occur in the sample. We shall take the diffusion coefficient for iron in MgO, 1×10^{11} cm² sec⁻¹ at 1100° C and 5×10^{-10} cm² sec⁻¹ at 1400° C ([9], p. 249), as the rate determining process for the growth of magnesioferrite precipitates. Other processes such as nucleation may be rate limiting, but taking the diffusion coefficient for compositional changes is usually conservative.

Step three is to estimate the necessary quenching rate; the rate required to freeze-in any sample changes within the limits of the observational resolution. With a constant cooling rate, the effective diffusion length during quenching is approximated as ([9], p. 443):

$$l \cong \left[\frac{R}{QT} (DT^2) \right]^{1/2} \quad (5)$$

By replacing the total diffusion length with the instrument resolution, x^{res} , and rearranging, the required cooling rate is given as:

$$\dot{T}^{\text{req}} = \frac{RDT^2}{Q(x^{\text{res}})^2} \quad (6)$$

where R is the gas constant and Q the activation energy for diffusion, 42 kcal mol⁻¹ for iron in magnesium oxide. Required cooling rates for the different observational methods at two different temperatures are shown in Table III. Markedly more rapid quenching rates are required for more close observation and for more rapid kinetics of change.

Step four is to calculate the maximum allowable

STEP ONE: estimate the resolution, x^{res} , of the examination procedure



STEP TWO: estimate the rate of structural change during quenching



STEP THREE: calculate the cooling rate required to "freeze-in" the high temperature structure



STEP FOUR: for the proposed quench medium, calculate the maximum sample thickness allowable



STEP FIVE: for the chosen sample thickness, calculate the temperature change during transfer – if too large, then adjust quenching parameters

Figure 3 Step-by-step procedure for determining the requirements for freezing in the high temperature equilibrium of a solid sample by quenching.

sample thickness. Either the sample itself or the surface heat transfer coefficient may limit the heat removal rate, so it is necessary to calculate the required sample thickness for both cases. The smaller calculated sample size must be used as it corresponds to the rate limiting step. Equations 1 and 3 have been rewritten to evaluate the sample thickness required to achieve the necessary quenching rate:

$$L^{\text{Newt.}} = \frac{h^Q(T_f - T_q)}{\rho C_p \dot{T}^{\text{req}}} \quad (7)$$

$$L^{\text{NN}} = \left[\frac{k(T_f - T_q)}{\rho C_p \dot{T}^{\text{req}}} \right]^{1/2} \quad (8)$$

TABLE III Required quenching rates to freeze-in magnesioferrite precipitation in MgO

Furnace temperature (° C)	Observational resolution	Quench rate required (° C sec ⁻¹)
1100	Optical microscope, $x^{\text{res}} = 0.5 \mu\text{m}$	0.36
1400	Optical microscope, $x^{\text{res}} = 0.5 \mu\text{m}$	26.5
1100	Electron microscope, $x^{\text{res}} = 10 \text{ nm}$	890
1400	Electron microscope, $x^{\text{res}} = 10 \text{ nm}$	6.6×10^4

TABLE IV Calculated sample half-thickness required for quenching into a bath of liquid nitrogen ($T_q = 77$ K)

Furnace temperature ($^{\circ}$ C)	Observational resolution	Sample half-thickness (cm)	
		Newtonian cooling (Equation 7)	Non-Newtonian cooling (Equation 8)
1100	Optical microscope, $x^{\text{res}} = 0.5 \mu\text{m}$	45	<u>6.4</u>
1400	Optical microscope, $x^{\text{res}} = 0.5 \mu\text{m}$	<u>0.75</u>	0.82
1100	Electron microscope, $x^{\text{res}} = 10 \text{ nm}$	<u>0.02</u>	0.13
1400	Electron microscope, $x^{\text{res}} = 10 \text{ nm}$	<u>0.0003</u>	0.02

As a quench medium, liquid nitrogen gives a rapid initial cooling rate, but then a gas film forms which slows the quench. As a result, thermal shock fracture is not often a problem. We have calculated the required sample thickness for quenching into liquid nitrogen as shown in Table IV. For each quench condition the smaller size is underlined. The half thicknesses range from 6.4 cm to $3 \mu\text{m}$. For the sample quenched from 1100° C for optical microscopy, a simple air quench would be satisfactory. The $3 \mu\text{m}$ half thickness necessary for a 1400° C quench for electron microscopy is completely unmanageable. Higher heat transfer coefficients can be obtained without thermal shock fracture by using liquid tin. In Table V we calculate the sample thickness required and find that a sample half thickness of $70 \mu\text{m}$, a practical sample thickness, is suitable for quenching a sample from 1400° C for electron microscope observation.

Step five is to determine if the temperature change during travel from the furnace to the quench bath is acceptable. For small sample sizes heat loss during the travel step may be excessive. For a sample dropping through still air the principal heat loss will be by radiation to a relatively low temperature and the rate of heat loss is ([6], p. 292):

$$j = \alpha \times 1.37 \times 10^{-12} T^3 \Delta T \text{ cal cm}^{-2} \text{ sec}^{-1} \quad (9)$$

giving an effective heat transfer coefficient $h = \alpha \times 1.37 \times 10^{-12} T^3$. Taking $\alpha = 1$ and the radiating temperature as the sample furnace temperature is

conservative, giving:

$$h_{\text{rad}} = 0.0028 \text{ at } 1000^{\circ} \text{ C}$$

$$0.0035 \text{ at } 1100^{\circ} \text{ C}$$

$$0.0044 \text{ at } 1200^{\circ} \text{ C}$$

$$0.0053 \text{ at } 1300^{\circ} \text{ C}$$

$$0.0064 \text{ at } 1400^{\circ} \text{ C}$$

$$0.0076 \text{ at } 1500^{\circ} \text{ C}$$

$$0.0090 \text{ at } 1600^{\circ} \text{ C}$$

Using these values and taking the ambient as 30° C, we calculate from Equations 2 and 4 for the proposed conditions, the values shown in Table VI. Cooling for most ceramics will be Newtonian during the transfer process, but it is better to calculate for both Newtonian and for non-Newtonian cooling and then use the smallest value of the two results which will be the limiting case.

From the results of Table VI we see that for the sample sizes appropriate for optical microscopy, the temperature changes during a simple drop transfer from the furnace to the quench bath are entirely satisfactory. However, freezing in changes on the scale observable with electron microscopy requires samples having a half thickness in the range 0.007 to 0.02 cm. For these sample thicknesses the temperature change during sample transfer is 50 to 140° C, much too large to describe as "freezing-in" a high temperature structure. Using a propelled insulating envelope method of sample transfer, the temperature changes during

TABLE V Calculated sample half-thickness required for quenching into a bath of liquid tin ($T_q = 850$ K)

Furnace temperature ($^{\circ}$ C)	Observational resolution	Sample half-thickness (cm)	
		Newtonian cooling (Equation 7)	Non-Newtonian cooling (Equation 8)
1100	Optical microscope, $x^{\text{res}} = 0.5 \mu\text{m}$	824	<u>4.1</u>
1400	Optical microscope, $x^{\text{res}} = 0.5 \mu\text{m}$	17.5	<u>0.60</u>
1100	Electron microscope, $x^{\text{res}} = 10 \text{ nm}$	0.33	<u>0.08</u>
1400	Electron microscope, $x^{\text{res}} = 10 \text{ nm}$	<u>0.007</u>	0.01

TABLE VI Temperature change during transfer of sample from furnace to quenching bath

Furnace temperature (° C)	Sample half-thickness (cm)	Temperature change (° C)	
		Newtonian (Eq. 2)	Non-Newtonian (Eq. 4)
(a) Using drop transfer through still air			
1100	6.4 (to N ₂)	0.13	<u>0.06</u>
1400	0.75 (to N ₂)	<u>2.5</u>	5.3
1100	0.02 (to N ₂)	<u>50</u>	> 200
1400	0.007 (to Sn)	<u>140</u>	> 200
(b) Using propelled sample transfer in insulating envelope as shown in Table I			
1100	6.4 (to N ₂)	0.01	<u>0.004</u>
1400	0.75 (to N ₂)	<u>0.15</u>	<u>0.32</u>
1100	0.02 (to N ₂)	<u>2.8</u>	> 200
1400	0.007 (to Sn)	<u>8.5</u>	> 200

transfer of 0.02 to 0.007 cm half thickness samples are about 2.8 to 8.5° C. These temperature changes limit the precision of defining the "frozen-in" temperature, but are in a range of practical utility for most high temperature research.

5. Conclusions

The quenching rate that can be achieved in solid materials is determined by the sample half thickness and the quenching medium. By using a sufficiently thin sample and a quenching medium with a high heat transfer coefficient, the high temperature structure can generally be "frozen-in". However, the temperature change during transfer of a very thin sample from furnace to quenching bath is excessive.

A propelled insulating envelope quench furnace is described with a fast sample transfer time that minimizes the temperature change during sample travel and allows successful quenching of thin samples. This raises the confidence in high resolution microstructure determinations for quenched solids.

Finally, a procedure is outlined to aid in the selection and evaluation of quenching processes. A sequence of steps is used that links the observational technique with the kinetics of change in the system such that no visible change occurs during quenching. This procedure can be applied

to any materials system to evaluate quench requirements and the need for rapid transfer systems, and to identify systems that must be examined *in situ*.

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