Solidification in Heat Packs: III. Metallic Trigger

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The metallic trigger used in commercial heat packs initiates solidification by releasing minute crystals of solid sodium acetate trihydrate into the subcooled solution. These crystals are harbored in submicron cracks on the disk's surface and are released when the disk is flexed. Using scanning electron microscopy, such seed crystals are observed on the surface of a disk after flexing it. Classic nucleation theory is used to investigate the behavior of crystals residing in the cracks on the metallic disk's surface during heating and cooling. Sodium acetate trihydrate crystals are capable of surviving in a 1-nm crack or smaller at regeneration temperatures of the order of 353 K. These seed crystals grow to the mouth of the crack at temperatures below the liquidus, but can only promote solidification of the whole solution surrounding the disk at temperatures below 256 K or when the disk is flexed.

Introduction

A heat pack consists of a sealed, flexible PVC envelope (typically 20×10 cm^2) containing a subcooled aqueous solution of sodium acetate (Araki et al., 1995; Ulman and Valentin, 1983). A metallic trigger located within the container initiates the solidification of the liquid to release latent heat (Kapralis et al., 1990). In Part I of this series of articles, we used classic nucleation theory to determine the pressure and temperature conditions under which solidification of an aqueous solution of sodium acetate occurs instantaneously. In Part II, we showed that cavitation promoted by the metallic trigger cannot induce solidification in a heat pack. The purpose of the present article is to investigate further the operation of the metallic trigger.

The metallic trigger used in commercial heat packs is a flexible stainless-steel disk about 20 mm in diameter. A photograph of the disk is shown in Figure 1. The disk has a pattern of indentations on its surface (Kapralis et al., 1990). The processes of stamping and stressing the metal to form these indentations also produce cracks around the edges of each indentation. The disk has one slightly concave and one slightly convex face. These faces can be reversed by a flexing action with the fingers. In normal use, the disk is immersed in the sodium acetate solution within the heat pack. Flexing the disk between the fingers triggers solidification, whereupon solid crystals grow from the indentations on the disk.

As we have seen in Part I, during the *regeneration* procedure, the disk is heated with the crystals. After the solution cools, the disk will trigger solidification again when flexed. The disk does not need to be flexed from one conformation to the other in order to trigger solidification. It only needs to be flexed slightly in either direction. This is why current heat packs are liable to be inadvertently activated when dropped or vibrated.

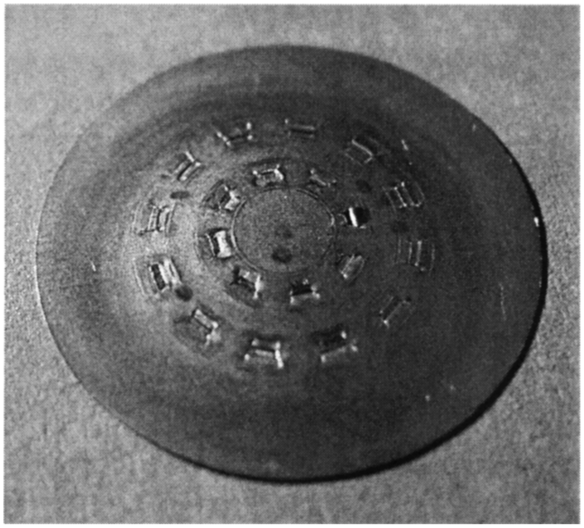

Figure 1. Metallic disk used in a heat pack.

In this article, we propose that the metallic disk initiates solidification by releasing minute crystals of solid sodium

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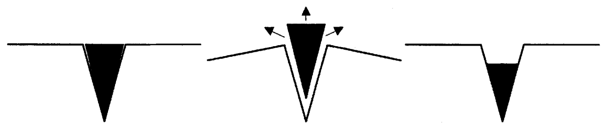


(*a*) Crack in the surface of an active disc containing a crystal.

(*b*) Crystal is ejected when disc is flexed, causing solidification.

(*c*) Crystal survives at high regeneration temperature.

Figure 2. Triggering mechanism.

acetate trihydrate into the solution when the disk is flexed. These crystals reside in the cracks on the disk's surface, and so do not cause crystallization prior to flexing. The interactions between the stainless steel and the crystals effectively raise their melting point such that they do not melt during the regeneration procedure. The minute crystals then grow in the cracks during the cooling process. These events are illustrated in Figure 2. We test this hypothesis theoretically and experimentally.

In the next section, classic nucleation theory is used to investigate the behavior of crystals residing in cracks on the metallic disk's surface during heating and cooling. We determine the *critical size* of sodium acetate trihydrate crystals growing in a stainless-steel cavity; crystals larger than the critical size are able to grow spontaneously out of the crack and cause solidification of the whole subcooled solution. We then develop a range of experiments to test our hypothesis. We discuss how the experimental evidence supports our hypothesis and refutes alternative mechanisms.

Theory

In this section, the classic theory of nucleation used in Part I, is generalized to heterogeneous nucleation on the surface of the metallic disk. The works of Gunton (1999), Oxtoby (1992), and Turnbull (1950) form the basis for this theoretical development, but a wider range of cavity shapes is considered here.

We use the theory to investigate two of the stages shown in Figure 2. First, we determine if stable crystals of sodium acetate trihydrate can exist in cavities at the high temperatures used in the regeneration process. This is possible if the free energy of the system has a minimum above the liquidus temperature, in particular at the temperatures reached during regeneration. Second, we show that a stable crystal contained in a small crack does not grow out of the cavity in the subcooled solution unless the disk is flexed.

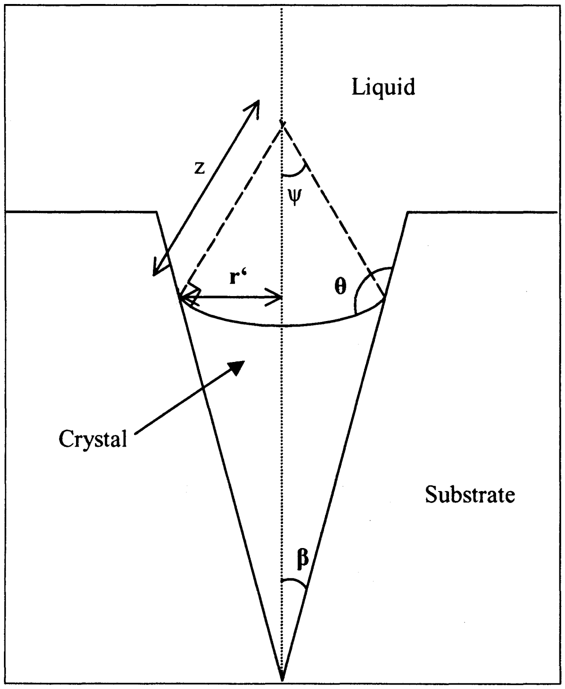


Figure 3. Parameters characterizing a concave crystal in a conical-shaped cavity.

We begin with an illustration of a conical-shaped crack and determine the conditions under which sodium acetate trihydrate crystals can be harbored in it. The parameters defining the size and shape of the crystal are shown in bold in Figure 3. These are the maximum horizontal radius of the crystal, r', the contact angle between the solution and the crystal, θ, and the half-angle at the apex of the cavity, β. For the crystal with a concave surface in Figure 3, $r' > 0$, $0 < \theta < 180°$, and $0 < \beta < 90°$. Two additional parameters are useful and can be derived from the preceding three primary parameters: the radius of curvature of the concave (or convex, not shown) surface of the crystal, z, and the half-angle of the segment of the sphere formed by this concave surface, ψ, where

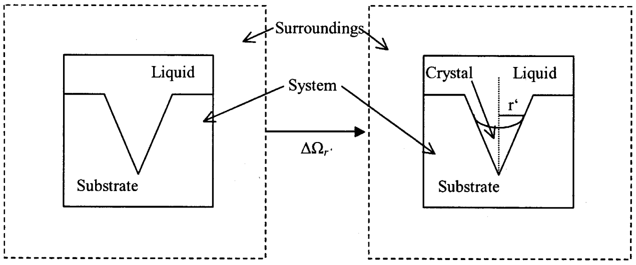
$$\psi = \theta - \beta - 90° \tag{1}$$

and

$$z = \frac{r'}{\sin \psi} \tag{2}$$

For a concave surface of the crystal, ψ and z are positive, while for a convex surface they are negative.

Consider the growth of a crystal in the conical-shaped cavity illustrated in Figure 4. The change in free energy between



State I: Size of crystal = 0

State II: Size of crystal = r'

Figure 4. Growth of a concave crystal in a conical-shaped cavity.

states I and II, $\Delta\Omega_{r'}$, is determined in an analogous way to that in Part I. The temperature and pressure of each phase in states I and II are taken to be T and p. The concentration of the solution or the volume of the system are not important, as was found to be the case in Part I. Similarly, the change in $\Delta\Omega_{r'}$ due to solution mixing effects is assumed to be negligible. The volume of the crystal, V, and the area of the surfaces between crystal and substrate, A_{cs}, and crystal and liquid, A_{cl}, each contribute to $\Delta\Omega_{r'}$ (Kashchiev, 2000; Kurz and Fisher, 1986)

$$\Delta\Omega_{r'} = A_{cs}(\sigma_{cs} - \sigma_{ls}) + A_{cl}\sigma_{cl} + V\Delta g_v \tag{3}$$

where Δg_v is the difference in the specific Gibbs free energy between crystal and liquid, σ is the surface energy, and the subscript ls refers to the interface between liquid and substrate.

Assuming mechanical equilibrium holds throughout the growth and shrinkage of the crystal, some simplification to Eq. 3 can be made by substituting the equation for mechanical equilibrium (Turnbull, 1950)

$$\sigma_{cs} = \sigma_{ls} + \sigma_{cl}\cos\theta \tag{4}$$

and Eq. 3 becomes

$$\Delta\Omega_{r'} = \sigma_{cl}(A_{cs}\cos\theta + A_{cl}) + V\Delta g_v \tag{5}$$

where A_{cs}, A_{cl}, and V may be determined geometrically

$$A_{cs} = \frac{\pi r'^2}{\sin\beta} \tag{6}$$

$$A_{cl} = \frac{2\pi r'^2}{\sin^2\psi}(1-\cos\psi) \tag{7}$$

$$V = \pi r'^3\left[\frac{1}{\tan\beta} - \frac{1}{\sin^3\psi}\left(2/3 - \cos\psi + 1/3\cos^3\psi\right)\right] \tag{8}$$

From Part I (Eq. 7), Δg_v for a crystal of sodium acetate trihydrate is given by

$$\Delta g_v(T,p) = \frac{(331+5p-T)\left\{152.5\left[(331+5p)^2+331^2\right]+1.09\times10^6(5p)+3.77\times10^8\right\}}{331+5p} - 152.5(331+5p-T)^2 + 1.09\times10^6\left[T\ln\frac{331+5p}{T} - (331+5p-T)\right] \tag{9}$$

where p is the pressure in kbar.

Substituting Eqs. 6–8 into Eq. 5 gives

$$\Delta\Omega_{r'} = r'^2 a\sigma_{cl} + r'^3 b\Delta g_v \tag{10}$$

where

$$a = \left\{\pi\left[\frac{\cos\theta}{\sin\beta} + \frac{2}{\sin^2\psi}(1-\cos\psi)\right]\right\} \tag{11}$$

and

$$b = \left\{\pi\left[\frac{1}{\tan\beta} - \frac{1}{\sin^3\psi}\left(2/3 - \cos\psi + 1/3\cos^3\psi\right)\right]\right\} \tag{12}$$

A minimum in $\Delta\Omega_{r'}$m occurs when $(d\Delta\Omega_{r'})/dr' = 0$ and $(d^2\Delta\Omega_{r'})/dr'^2 > 0$. From Eq. 10, we have

$$\frac{d\Delta\Omega_{r'}}{dr'} = 2r'a\sigma_{cl} + 3r'^2 b\Delta g_v \tag{13}$$

Even though the case described is for a conical-shaped cavity, the result for the derivative of the free energy, $(d\Delta\Omega_{r'})/dr'$ given in Eq. 13, will hold for any axisymmetric-shaped cavity for which r' is monotonically increasing. Setting $(d\Delta\Omega_{r'})/dr' = 0$ gives the critical size of the crystal, r'^*

$$r'^* = \frac{-2a\sigma_{cl}}{3b\Delta g_v} \tag{14}$$

Setting the second derivative to greater than zero

$$\frac{d^2\Delta\Omega_{r'}}{dr'^2} = 2a\sigma_{cl} + 6r'b\Delta g_v > 0 \tag{15}$$

gives

$$2a\sigma_{cl} + 6r'^* b\Delta g_v > 0 \tag{16}$$

and substituting for r'^* from Eq. 14 gives

$$-2a\sigma_{cl} > 0 \tag{17}$$

Equation 17 shows that a must be negative for a minimum to exist in $\Delta\Omega_{r'}$ because σ_{cl} is defined as positive. Equation 14 shows that when a is negative, b must be positive when Δg_v is positive and negative when Δg_v is negative for a minimum to exist in $\Delta\Omega_{r'}$; Δg_v is negative in the subcooled state and positive during the regeneration process.

Analysis of Eqs. 10 and 11 shows that $a < 0$ when $\psi > 0$ and $b > 0$ when $\psi > 0$. This implies that a stable crystal can only exist within the cavity above the liquidus temperature.

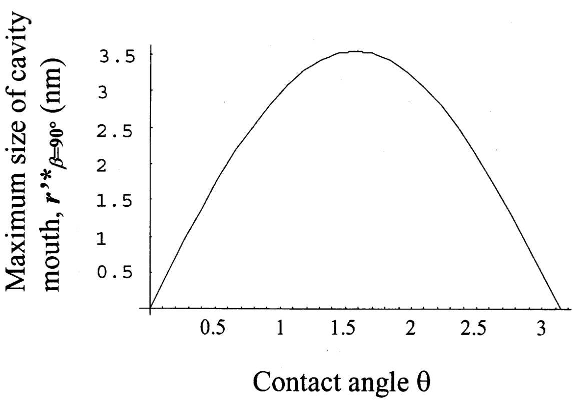


Figure 5. Maximum size of the cavity mouth, $r'^*_{\beta=90°}$, for crystals to remain stable at 294 K as a function angle θ.

At regenerating conditions of 80°C and 1 bar, r'^* is calculated from Eq. 14 to be of the order of 1 nm.

To further investigate the stability of crystals in differently shaped cavities, one cavity with walls described by r'^2 and another with walls described by $\sqrt{r'}$ were analyzed numerically from Eq. 13 using *Mathematica.* Both of these cavity shapes were also only able to harbor crystals above the liquidus temperature but not below it. In addition, the latter case was only able to harbor crystals when the contact angle $\theta > 90°$.

We conclude then that when the heat pack cools below the liquidus temperature, the crystal grows to fill the cavity. However, it will cease to grow further and cause solidification of the solution unless the radius of the mouth of the crack, r', is greater than the critical size needed for nucleation on a flat substrate. This critical value is given by Eq. 14 when $\beta = 90°$ and represents a maximum in the free energy of the system

$$r'^*_{\beta=90°} = \frac{-2\sigma \sin\theta}{\Delta g_v} \tag{18}$$

The maximum cavity size for crystals to remain stable during subcooling is a function of the liquid–crystal contact angle for sodium acetate trihydrate on stainless steel, θ, which is unknown. The variation of $r'^*_{\beta=90°}$ with θ is shown in Figure 5, for typical subcooled conditions in the pack of 294 K and 1 bar. The critical size has a maximum of 3.5 nm at $\theta = 90°$. At a temperature of 256 K, $r'^*_{\beta=90°}$ has a maximum value of 1.75 nm. We can, therefore, expect that as the temperature is reduced below the liquidus, heat packs containing the metallic trigger will solidify readily before those without the metallic disk.

When a disk is flexed, crystal growth is promoted by ejection of the crystal from the crack and exposure of the sides of the crystal or simply by stretching the mouth of the cavity to become greater than the critical size.

Experimental Procedure and Results

A range of experiments was carried out to investigate the mechanism by which the metallic disks trigger solidification. The disks used here were obtained new from the manufacturer. These experiments are described below.

Sodium acetate solution

The sodium acetate solution was prepared from sodium acetate trihydrate crystals (Rectapur 98% pure) and distilled water. The solution was placed in translucent cadmium-free PVC pouches (10 cm × 10 cm) open at one of the shorter sides into which the disks could be inserted or removed with plastic tweezers (this was a standard sized heat pack cut in half). To minimize evaporation of the water in the solution, the open end of the pack was kept sealed by folding over the PVC and keeping it clamped at all other times.

After crystallization was triggered using a metallic disk, the solution was heated by suspending the closed end of the pack in a hot-water bath at about 85°C, and cooled to room temperature (approximately 20°C) by suspending it in an iced-water bath.

Preliminary experimental observations

A number of important observations were made from our preliminary experiments on the ability of a disk to trigger solidification of the subcooled solution. These observations were relevant to the planning of further experimental work, and, hence, we state them at this stage. The following was noted.

(a) Each Disk Behaves the Same as Any Other. Many different disks were used in the experiments and marks were placed on each disk and a record kept of which disk was used in which experiment. No consistent difference was ever noted between the results obtained with any particular disk. The results were, therefore, aggregated and no mention is made of which individual disk was used in the results below.

(b) A Disk Does Not Retain a Memory of Its Past Treatment. Except for the first few nucleations after a disk has become reactivated (see below) no evidence was ever noted of the results being dependent on a disk's history (for example, how many times it had been deactivated in the past). Therefore, no mention is made of this in the results below.

(c) The Cooling Rate of the Solution Does Not Affect the Activity of a Disk. Experiments were carried out in which the solution was left to cool at a very low rate (immersed in a large body of hot water), in air at room temperature, and in iced water. No differences in the subsequent activity of the disk were noted, and consequently cooling of the solution in iced water was used in all subsequent experiments, as it was the fastest process.

(d) The Activity of a Disk Is Independent of the Precise Concentration of the Sodium Acetate Solution. In the preliminary experiments, the concentration was varied between $x = 0.170$ and $x = 0.210$ mole fraction of sodium acetate trihydrate in water. No effect of the concentration on the activity of a disk was noted. We, therefore, carried out all experiments on a standard solution with $x = 0.206$ (unless otherwise stated), which is sufficient to prevent the formation of sodium acetate anhydrite (see Part I).

Activation and deactivation of a disk

A set of experiments was carried out to identify procedures by which a disk can be activated and deactivated. In what follows, the term "hot" means approximately 85°C and the term "cold" means room temperature (approximately 20°C).

Importance of Surface Cracks on the Disk. The cracks on the disk's surface are necessary to trigger solidification. A two-stage process forms the cracks during manufacture. First, indentations are made by stamping one side of the disk. Second, these indentations are flattened by stamping the other side of the disk; this cracks the surface of the metal as it folds back. Disks that have only been indented do not cause nucleation.

Deactivation of a Disk by Flexing It in a Hot Liquid. A disk can be made inactive by repeatedly flexing it while it is immersed in hot sodium acetate solution (for example, during the regeneration procedure) or when immersed in hot water. We define a deactivated disk as one that will not trigger solidification when flexed 20 times in the cold solution. The results of deactivation by flexing are shown in Table 1.

Great care was taken to ensure that the procedure developed for taking the disk out of solution does not affect the properties of the disk (see below). The deactivation process is over 80% effective in hot solution and hot water after flexing the disk 30 times. The process is less effective when the disk is flexed fewer times. In the instances where a disk remained active, crystals grew from a few distinct places in the cracks rather from several hundred places, as in a disk that we had not attempted to deactivate. These experiments suggest that there are a number of sites in the cracks that will cause nucleation when the disk is flexed and each successive flexing in hot solution or water increases the probability that a given site will be deactivated.

Reactivation by Exposure to Crystals. A deactivated disk can be reactivated if the solution in which it is immersed is solidified. After the crystals have been dissolved during the regeneration procedure and the solution cooled, the disk can trigger solidification when it is flexed. However, this process of solidification around the disk sometimes needs to be repeated more than once. Disks reactivated in this way always remain active until deactivated again. The reactivation results are shown in Table 2.

The reactivation procedure is about 50% reliable for initially inactive disks, and 100% reliable for maintaining the activity of initially active disks. It was noted that the crystal growth during the triggering of a newly reactivated disk occurred from only a few sites, but in the second nucleation hundreds of sites were active. These experiments suggest that each time an inactive disk is exposed to solidification of the surrounding solution, there is a probability that the potential sites for nucleation will become activated.

Heating several inactive disks in sodium acetate solution to the same temperature and for the same length of time as during regeneration did not result in any of these disks becoming active. Hence, the processes of heating and cooling of the disks during the regeneration procedure are ruled out as the cause of reactivation.

Activity of Virgin Disk. We have seen that a deactivated disk can be reactivated by solidifying the solution in which it is immersed. This suggests that virgin disks, which have not been exposed to sodium acetate, may be inactive. A sample 15 virgin disks was obtained from the manufacturer. The surface of seven of those tested was rinsed with distilled water before immersion in a cold solution, and the remaining eight were placed in a hot solution, which was then cooled. In both cases, only about 50% of these disks were found to be inactive; we believe that the disks that were active had become contaminated with solid sodium acetate trihydrate during or after manufacture. This explanation is supported by the fact that four out of an additional five new disks that were placed directly into cold solution (without rinsing) had something (presumably crystals of sodium acetate trihydrate) on the surface that caused nucleation before the disk was flexed. The properties of new disks are shown in Table 3.

Effect of the Removal Procedure. The removal procedure adopted in all experiments consisted in removing the disk from the cold solution by gripping it on the very edge with plastic tweezers. As soon as it was removed from the solution, both sides of the disk were rinsed twice with distilled water at room temperature (moving the position of the tweezers between the rinsings). Water adhering to the surface was shaken off and the disk was placed on a wire rack to dry in air at room temperature for 12 h. Contamination from airborne particles during this time was minimized by covering the disk with a cover of aluminum foil (the cover did not touch the disk).

It is desirable that the removal procedure does not change the state of a disk: disks that were active would remain active when replaced in solution and those that were inactive would remain inactive. Unfortunately, a procedure was not found that was always reliable, and it is concluded that the process of removing disks from solution, rinsing them with distilled water, and then drying them in air can cause deactivated disks to become active but not vice versa. The results are summarized in Table 4.

Deactivation by Heating in an Oven. The melting temperature of sodium acetate trihydrate is 58°C. Our hypothesis suggests that active disks could be deactivated by heating to a sufficiently high temperature to melt the crystals in the cracks. This experiment consisted in heating active disks to 250°C in an oven. The results are summarized in Table 5. The incidence of deactivation is not sufficient to conclude that deactivation by heating occurs. The oven temperatures are much higher than the melting temperature of sodium acetate trihydrate, but it is possible that crystals retained in the cracks

Table 1. Results for Deactivation in a Hot Liquid

No. of Disks Tested	Immersion Fluid	No. of Flexes	No. of Deactivated Disks	Deactivated Disks
16	Hot solution	30	13	81%
6	Hot water	30	5	83%
3	Hot solution	5	2	67%

Table 2. Results for Reactivation by Exposure to Crystals

	No. of Times Surrounding Solution was Solidified	No. of Activations	Reactivation Rate
Initially inactive disks	23	12	52%
Initially active disks	> 50	> 50	100%

Table 3. Activity of Virgin Disks

No. of New Disks Tested	Treatment	No. of Disks Causing Nucleation in Cold Solution	Disks Causing Nucleation
7	Rinsing surface with cold water	3	43%
8	Placing in hot solution	4	50%
5	None	4 (without flexing)	80%

will have a higher effective melting temperature. Further work would be required to determine whether the crystals do not melt or melt and then resolidify.

Imaging of the disk's surface with a scanning electron microscope

A set of experiments was carried out to examine in detail the surfaces of metallic disks. A JSM-5800 scanning electron microscope (SEM) capable of elemental sample composition determination by X-ray analysis was used. Accelerating voltages of between 4 and 20 keV were used. The surfaces of disks were not treated or coated prior to imaging with the SEM.

We have seen earlier that the procedure for removing a disk from the solution is not 100% effective in maintaining inactive disks as inactive. Therefore, the inactive disks used in this set of experiments were tested for inactivity in a cold solution after observation on the microscope. Six disks were examined in total: three active disks, two inactive disks, and one supposedly inactive disk that actually caused solidification when it was later placed into the solution (without flexing). Each of the six disks was examined both before and after being flexed. The results are summarized in Table 6.

Two key findings can be drawn from the observations in Table 6. First, there are many more small particles on the surface of an active disk than on the surface of an inactive disk, after flexing. Second, large particles were observed on the surfaces of both active and inactive disks, but those on the active disks contained a higher proportion of sodium. Figure 6 shows images of the large crystals, rich in sodium, found on the surface of two of the active disks. The composition of these crystals is predominantly Na, C, O, and Si. Exact elemental ratios could not be determined, however, because the light elements (C, O, H) cannot be quantified reliably.

Unfortunately, the composition of the small particles could not be determined using the X-ray analysis facility on the SEM; these particles were so small that the signal was swamped by the response from the stainless-steel disk itself.

Table 4. Effect of Removal

State Before Removal	No. of Disks	No. with State Unchanged After Removal	State Unchanged After Removal
Inactive	17	9	53%
Active	20	20	100%

Table 5. Effect of Heating in an Oven

No. of Active Disks Tested	Temp.	Duration	No. of Disks Becoming Inactive	Disks Becoming Inactive
3	150°C	1 h	1	33%
3	250°C	1 h	0	0

Flexing a disk over a sodium acetate solution

This experiment consisted of flexing both inactive and active disks over an open beaker of sodium acetate solution. Three active disks and two inactive disks were tested and the results are summarized in Table 7.

The results show that flexing an active disk over an open beaker of sodium acetate solution causes the solution below to crystallize, whereas flexing an inactive disk in the same way does not.

Effect of low temperature

Two heat packs were placed in a freezer at a temperature of 256 K. One of the packs contained a metallic disk in the sodium acetate solution, while the other did not. We observed that the solution in the pack containing the metallic disk solidified after 24 h in the freezer. The solution in the pack without the metallic disk remained liquid after one week in the freezer. The experiment was repeated three times and the same results were obtained each time.

Discussion

Our hypothesis is that the active disks contain minute crystals in their cracks and the inactive disks do not. We showed

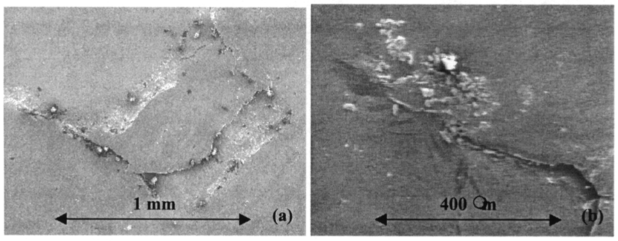
Table 6. SEM Imaging Results

	Type of Disk Tested (n = No. Tested)		
Observations	Active Disks ($n = 3$)	Inactive Disks Becoming Inactive Later ($n = 2$)	Inactive Disks Becoming Active Later ($n = 1$)
No. of large particles (5–100 μm) before flexing[*]	Many	Many	Many
After flexing	Many	Many	Many
No. of small particles (< 5 μm) before flexing[**]	Few	Few	Few
After flexing	Many	Few	Few
Main shapes of large particles	Needle and amorphous	Needle and amorphous	Needle, amorphous and plate
Sodium in large particles. Also containing: C, O, K, Cl, Cr, Al, Ca[†]	30–80%	1–50%	1–50% Plate—unknown (too thin to be sampled)

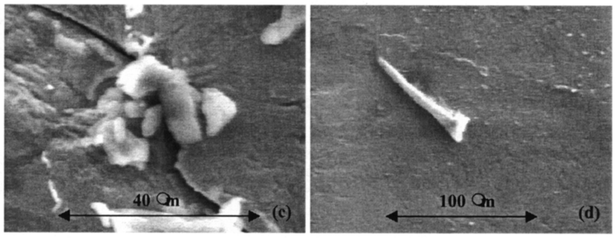
[*] Each disk had many large particles on its surface (between 50 and 100). Excludes dirt particles.

[**] Few small particles means 10–50 around each machine mark; many means 100 or more.

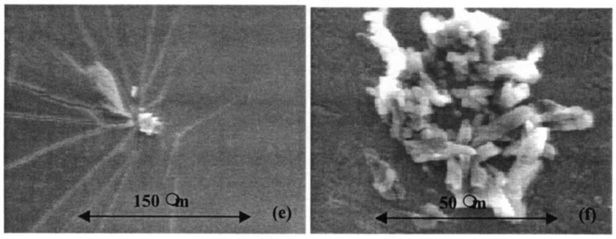
[†] Each disk also contained many large, predominately carbonaceous (dirt) particles.



(*a*) cracks and particles surrounding one of the 20 indentation marks.   (*b*) particles surrounding a crack.



(*c*) higher resolution image of (*b*).   (*d*) lone needle like particle.



(*e*) crystal growth into shallow cracks.   (*f*) cluster of crystals in an indentation on the surface.

Figure 6. Scanning electron microscope images of cracks and crystals on the surface of an active disk (a)/(e) before flexing, and (f) after flexing.

theoretically that such crystals are able to survive in the cracks at the high temperatures used during regeneration, and that when the solution is cooled below the liquidus temperature, such crystals grow to the mouth of the crack but not beyond. These crystals will only be able to grow out of the crack and induce solidification of the whole solution surrounding the disk when the temperature is sufficiently low. Experimentally, we could not look directly into a crack on a disk. We, therefore, carried out a range of experiments to gather indirect evidence to test our hypothisis.

Our imaging experiments using a SEM showed that active disks contain a larger number of small particles on their surface than inactive disks, after flexing. This large number of small particles does not seem to arise as a result of the breakup of large particles during flexing, because the number of large particles present on the surface of both active and inactive disks is similar. We believe that these small particles are (or contain) crystals of sodium acetate trihydrate that are ejected from the cracks and act as seeds for nucleation when the disk is flexed. It is thought unlikely that another substance that could act as a seed for sodium acetate trihydrate would be present. Unfortunately, the elemental composition of the particles could not be verified using X-ray analysis.

Table 7. Effect of Flexing a Disk Over Sodium Acetate Solution

	No. of Disks Tested	No. Causing Nucleation	Causing Nucleation
Active disks	3	2	67%
Inactive disks	2	0	0

Our experiments on the activation and deactivation of a disk showed that

(1) The cracks on the surface of a disk are crucial to its activity.

(2) A disk can be deactivated by flexing it a large number of times in hot solution or hot water.

(3) A disk can be reactivated by making the solution in which it is immersed solidify.

(4) Virgin disks are less active than disks that have previously been exposed to solidification.

These results suggest that minute crystals of sodium acetate are indeed contained in the cracks of an active disk. Some of these crystals are ejected from the cracks each time the disk is flexed. In hot solution or water, the ejected crystals melt, and if all seeds are released from a disk in this manner, it becomes inactive. To reactivate it, new seed crystals need to lodge in the cracks of the disk. This is achieved by making a solution solidify around the disk. Virgin disks should not contain sodium acetate crystals in their cracks, and, hence, are less likely to cause solidification.

By flexing a disk over a subcooled solution of sodium acetate, we showed that active disks can cause the solution to solidify, while inactive disks do not. These observations suggest that minute crystals of sodium acetate contained in the cracks of an active disk can drop out when the disk is flexed, whereas none drop out from an inactive disk. Such behavior is in accord with our theoretical predictions.

We also showed experimentally that at a sufficiently low temperature of 256 K, a solution containing a metallic disk solidifies without flexing the disk. A solution in which no disk is immersed does not solidify at this temperature. These observations are supported by the theory, which suggests that as the temperature decreases, the critical radius above which a crystal can grow out of the mouth of the crack decreases. At 256 K, the critical radius has a maximum value of 1.75 nm. Thus, if the mouth of a crack containing a crystal is larger than approximately 1.75 nm, solidification should occur in the presence of the disk, but not in its absence.

Conclusions

The metallic trigger used in commercial heat packs has a pattern of indentations on its surface (see Figure 1). Around the edges of each indentation, there are submicron cracks. The present work shows that the metallic disk operates by harboring crystals of sodium acetate trihydrate within the cracks on its surface. These minute crystals are released to seed the solution when the disk is flexed. Direct observation of what is believed to be such seed crystals was made on a disk, after flexing it, using a SEM.

We were able to deactivate a disk by removing all seed crystals from its cracks, and conversely, an inactive disk was made active by ensuring that seed crystals were present in its cracks.

Our theory supports the experimental results. Crystals were shown to be capable of surviving in cavities at regeneration temperatures of the order of 85°C. These seed crystals grow to the mouth of the cavity when the solution is cooled to temperatures below the liquidus temperature, but only will be able to grow out of the crack and induce solidification of the whole solution surrounding the disk when the temperature is sufficiently low.

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