

# Shape Memory Polymer (SMP) Venting Mechanism for Munitions

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## ABSTRACT

Cornerstone Research Group (CRG) is currently executing a Small Business Innovation Research (SBIR) Phase II program, sponsored by the U.S. Missile Defense Agency (MDA), to develop and demonstrate a thermally activated venting system as a slow cookoff mitigation device for solid rocket motors and munition containers. In the six-month Phase I effort in 2006, CRG successfully demonstrated the feasibility of a motor venting concept using a shape memory polymer (SMP) composite actuation device. The initial venting system design concept is presented, along with Phase II design refinements and plans for prototype slow cookoff testing.

## INTRODUCTION

Cornerstone Research Group (CRG) is developing temperature-activated pressure venting mechanisms using shape memory polymer (SMP) to meet cookoff requirements for ammunition containers and solid rocket motor cases. SMPs are polymers whose qualities have been altered to give them dynamic shape “memory” properties. Under thermal stimuli, SMP can exhibit a radical change from a rigid thermoset to a highly flexible, elastic state. SMP-based pressure venting mechanisms, coupled with conventional impact resistant containers or composite solid rocket motor cases, will offer failsafe IM solutions to rocket motor and munition designers.

In a Phase I SBIR effort, CRG demonstrated the feasibility of an SMP-actuated venting system designed to relieve confinement in a rocket motor or munition container subjected to a slow cookoff environment. In CRG’s venting design, an SMP composite provides the triggering mechanism for releasing containment at a specified temperature. At normal operating temperatures, the tension of the SMP composite keeps the mechanism in place. In a cookoff scenario, at a specified threshold temperature, the SMP’s activation temperature is exceeded, causing it to actuate in a controlled manner, allowing the mechanism to release and the case/container internal pressure to be vented.

CRG constructed a prototype SMP-actuated pressure venting mechanism based on an internal retaining ring design. CRG successfully tested the prototype venting mechanism in a thermal environment. When heat was applied to the nozzle assembly, the SMP ring returned to its memory shape, allowing the nozzle to be released from the aft closure as designed. In a two-year Phase II SBIR effort, the internal ring design concept will undergo prototype testing on an analog solid rocket motor in a full-scale slow cookoff test in accordance with NATO Standard Agreement (STANAG) 4382.

## SHAPE MEMORY POLYMER

At the forefront of shape memory polymer technology, CRG has been researching SMP since 1998 under the tradename Veriflex<sup>®</sup>. First introduced in the United States in 1984, SMPs are polymers whose qualities have been altered to give them dynamic shape “memory” properties. Under thermal stimuli, SMP can exhibit a radical change from a rigid polymer to a very flexible elastic state, then return to a rigid state. In its elastic state, SMP will recover its “memory” shape if left unrestrained. The “memory,” or recovery, quality comes from the stored mechanical energy attained during the reconfiguration and cooling of the material. SMP’s ability to change stiffness, modulus, and shape configuration makes it ideal for applications requiring lightweight, dynamic, adaptable materials.

Unlike a shape memory alloy (SMA), SMP exhibits a radical change from a normal rigid polymer to a very flexible elastic and back on command, a change that can be repeated without degradation of the material properties. The SMP transition process is a thermo-molecular relaxation, differing from SMA’s thermally-induced crystalline phase transformation. In addition, SMP demonstrates a much broader range and versatility than SMA in shape configuration and manipulation. SMP is not simply an elastomer, nor simply a plastic. It exhibits characteristics of both materials, depending on its temperature. While rigid, SMP demonstrates the strength-to-weight ratio of a rigid polymer; however, normal rigid polymers under thermal stimulus simply flow or melt into a random new shape; they do not exhibit a “memorized” shape to which they can return. While heated and pliable, SMP has the flexibility of a high-quality, dynamic elastomer, tolerating up to 200% elongation; however, unlike normal elastomers, SMP can be reshaped or returned quickly to its memorized shape and subsequently cooled into a rigid plastic.

Figures 1 and 2 show the initial range of CRG’s patented styrene-based Veriflex family of materials. Figure 1 shows the elastic modulus of SMP in relation to temperature, while Figure 2 shows the SMP’s storage modulus (stiffness) as a function of temperature. Note the sharp transition over a relatively short temperature range, which provides Veriflex with its unique properties and potential applications.

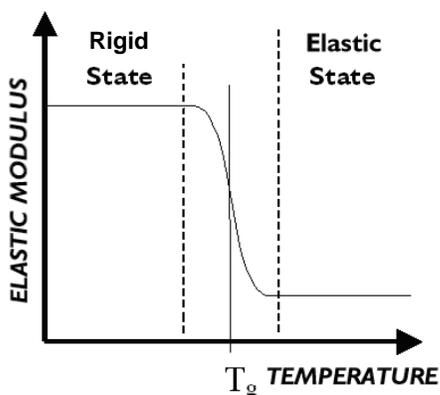


Figure 1. Veriflex elastic modulus versus temperature

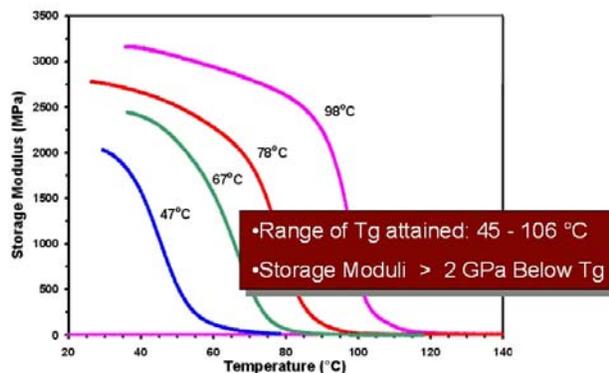


Figure 2. DMA graph of various styrene Veriflex storage moduli

In the SMP market, there are three types of SMP polymers: 1) partially cured resins, 2) thermoplastics, and 3) fully cured thermoset systems. In several years of research, CRG has found limitations and drawbacks to the first two types of SMP. Partially cured resins continue to cure during operation and change properties with every thermal cycle. Thermoplastic SMP

“creeps,” which means it gradually “forgets” its memory shape over time. With this supporting research and a thorough understanding of the chemical mechanisms of SMP polymers, CRG has developed fully cured, high-performance thermoset systems.

Above its transition temperature, in its elastic state, SMP will recover its “memorized” or cured shape very quickly if left unrestrained, a quality useful in deployment applications. In addition, while heated and pliable, it can be stretched, folded, rolled, twisted, bent, or otherwise reconfigured or manipulated into other shapes. Veriflex can be cooled to maintain its altered shape for as long as necessary until heated above its transition temperature. This thermal reconfiguration process can be repeated without losing material integrity. Both the memorized shape and the manipulated reconfigurations of the Veriflex will maintain shape integrity over time below transition temperature.

Veriflex currently functions on thermal activation that can be tailored from -25°C to 270°C. Figure 3 illustrates the variety of tailored SMP polymers in the intermediate and high temperature ranges likely to be applicable to solid propellant rocket motor applications. Extremely high temperatures and cryogenic ranges may also be possible. CRG has the capability to tailor polymers with shape memory properties, and has successfully accomplished this using acrylate, styrene, epoxy, maleimide and cyanate esters. Veriflex is only as exotic as the base polymer from which it was derived. It is also cost-effective. Styrene Veriflex, for example, would cost no more in bulk than any other high-performance composite resin system.

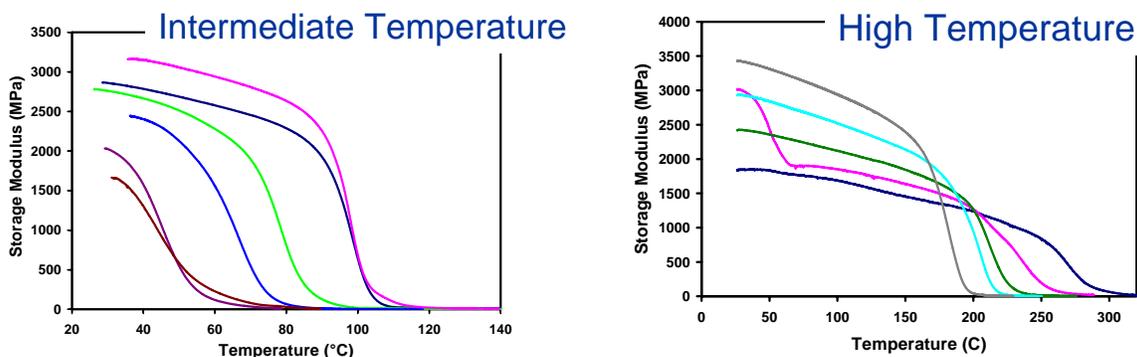


Figure 3. Examples of tailored SMP polymers in the expected range of useful activation temperatures for solid propellant rocket motors

An engineered polymer with shape memory characteristics provides a unique set of material qualities and capabilities that enhance traits inherent in the polymer system itself. Veriflex can be chemically formulated with a transition temperature to match any application need. It can be cast and cured into an enormous variety of “memorized” shapes, from thick sheets and concave dishes to tiny parts or a complicated open honeycomb matrix.

### SMP VENTING CONCEPT

Shape memory polymers (SMP) combined with traditional composite materials offer high strength-to-weight ratios, similar to other composites. However, SMP composites offer a unique ability to release stored mechanical energy at a predetermined temperature range. Veritex™, CRG’s SMP composite material, is like other high-performance composites, except CRG’s SMP, Veriflex, is the resin used as the matrix. Fabrication with Veriflex resin allows easy manipulation of the composite above the activation temperature and provides high strength and

stiffness at lower temperatures. The composite acquires some characteristics of Veriflex, making it a unique material for use in dynamic structures and other applications requiring both load strength and “shape-changing” flexibility. This unique set of mechanical properties makes SMPs and SMP composites ideal for implementing IM-compliant, lightweight, hybrid-composite, mechanisms for munition containers and solid rocket motor cases.

The goal of the Phase I program was to demonstrate the feasibility of an SMP-based IM venting system. In support of this goal, CRG conducted the following tasks:

- Requirements assessment
- Development of general device mechanism concepts
- Evaluation of general concepts
- Downselection to a single concept for prototyping
- Selection of appropriate SMP materials
- Development of specific device design
- Fabrication of device prototype
- Characterization of prototype and feasibility assessment

Design requirements for a rocket motor venting system, such as desired activation temperature, dimensional envelope, environmental considerations, and mechanical properties, were determined in consultation with the MDA technical monitor and an industry partner from the propulsion community.

Several venting concepts that utilized SMP’s unique set of mechanical properties as the means of actuation were conceived and evaluated. Two of the seven concepts considered are shown in Figure 4.



Figure 4. Vent design concepts evaluated included Turn & Lock (left) and Plug (right) concepts

The following downselect criteria were used during the evaluation of candidate designs:

- Design to limit load carried by polymer
- Adequate amount of venting available from release of mechanism
- Internal location of device, to limit interference with external interfaces
- Ease of integration into current and future systems

After considering the practicality and functionality of the candidate designs, in consultation with CRG’s industry partner, an internal retaining ring concept was chosen for the Phase I

prototype demonstration. Depicted in Figures 5 and 6 is the SMP internal retaining ring concept that was developed during the Phase I effort. The memory shape of the SMP composite ring is a smaller diameter (see Figure 7). In the mechanism, a ring of SMP composite would provide the triggering mechanism for releasing containment at a specified temperature. At normal operating temperatures, the shape of the SMP composite ring keeps the three-piece metal ring in contact with the aft boss. During slow heating, when the threshold temperature specified by the determined IM requirements is reached, the SMP's glass transition temperature ( $T_g$ ) is exceeded and the ring actuates in a controlled manner (rather than simply melting). The ring returns to the smaller memory shape and allows the system to vent.

The metallic three-piece ring is the primary structural element in the system, with the SMP composite ring solely used to keep the metal ring in place throughout normal operation. In this design, if the SMP is damaged or fails, the pressure is released; therefore, the design is fail-safe. Figure 8 shows the actual prototype fabricated during Phase I.

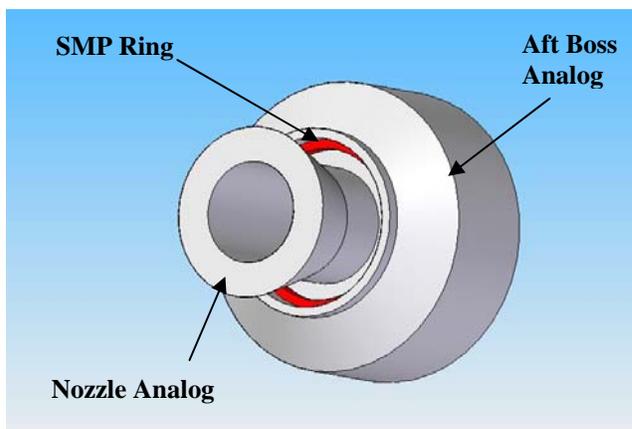


Figure 5. SMP internal retaining ring concept

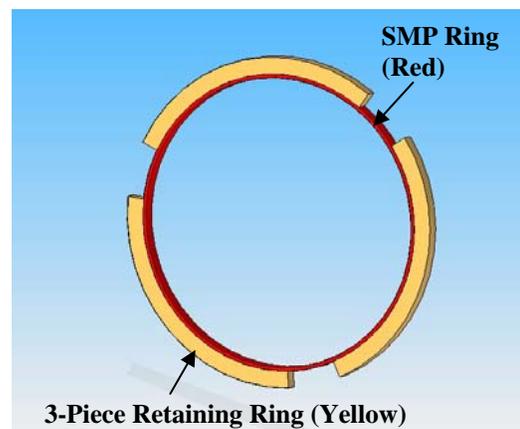


Figure 6. Retaining ring configuration



Figure 7. Comparison between expanded and memory shapes of SMP composite ring

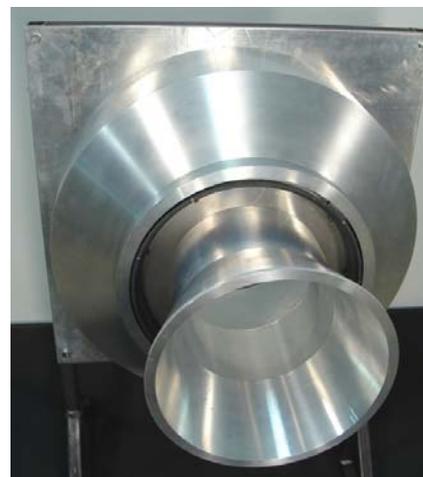


Figure 8. Phase I prototype test assembly

### CONCEPT FEASIBILITY TESTING

As shown in figure 8, an analog rocket motor nozzle assembly was fabricated, and the prototype internal retaining ring venting device was installed as designed. For Phase I feasibility testing, the SMP composite ring was fabricated using styrene-based SMP, allowing activation by a portable heat source.

The SMP composite ring was expanded to the desired diameter and attached to the three-piece metallic retaining ring, as shown in Figure 9.



Figure 9. Attachment of SMP composite ring to three-piece metallic retaining ring

Feasibility of the internal retaining ring design was successfully tested using a portable heat source to simulate an external heating scenario. During heating, the SMP composite ring retracted as designed. Close-up, post-test photos of the analog nozzle and the venting ring assembly following release are presented in Figure 10.



Figure 10. Released nozzle (left) and activated retaining ring (right)

## PHASE II PROTOTYPE DESIGN AND EVALUATION

A prototype configuration was chosen for integration and testing of CRG's thermally activated IM venting technology during the Phase II effort. The prototype rocket motor is a standard 7" ID test bottle consisting of a filament-wound, carbon fiber-reinforced polymer composite case. This test bottle has a significant legacy database of IM test results for various propellants and mitigation concepts. The test motor configuration will permit demonstration of CRG's fail-safe IM venting technology during a full-scale, NATO Standard Agreement (STANAG)-compliant slow cook-off test. The existing database will facilitate comparison of slow cook-off results with and without IM venting technology, permitting quantitative conclusions about the effectiveness of CRG's implemented IM solution. Results can also be directly compared with those of identical motors featuring other IM mitigation concepts.

Modification of the rocket motor's aft closure was required in order to accommodate CRG's IM venting mechanism. Several concepts for venting the motor by releasing the aft closure were evaluated by trading off the following criteria:

- ease of integration with test bottle motor case
- reliability
- passive thermal activation
- ease of fabrication
- amount of venting provided
- ability to survive normal operational conditions

The selected concept is shown in Figure 11. The SMP venting ring mechanism is located in the aft closure's retaining ring groove, holding in place the internal portion of the two-piece closure.

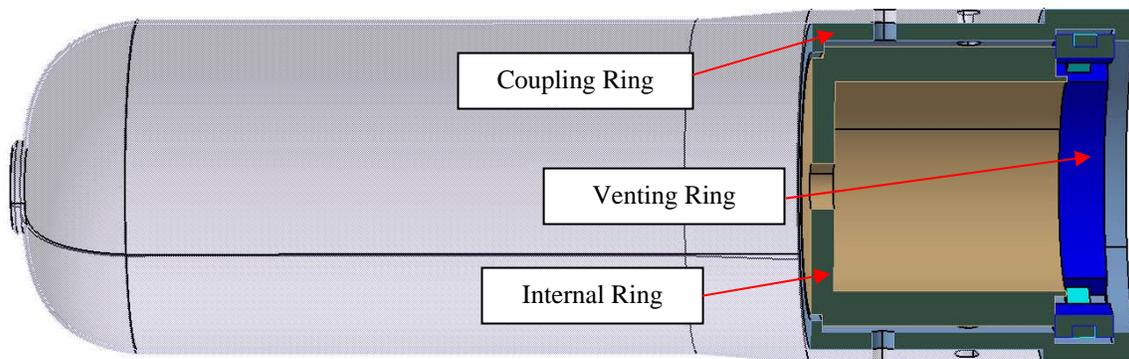


Figure 11. Test motor case with modified aft closure

The modified aft closure is a two-piece design, consisting of an outer coupling ring, which is attached to the motor case using the standard pins, and an internal cylinder that is held in place by the SMP-activated retaining ring. The forward face of the internal cylinder has an orifice sized to simulate the nozzle throat area that would be required to provide the design chamber pressure. When activated in a slow cookoff scenario, the retaining ring allows the internal portion of the aft closure to be expelled from the motor.

Design of the SMP-activated retaining ring has evolved since Phase I, incorporating several improvements. The Phase II concept, illustrated in Figure 12, consists of an SMP composite ring in its expanded shape, located in a three-piece metal channel. This entire

assembly is fitted into the retaining ring groove in the aft closure, holding the two-piece closure in place prior to thermal activation. This new design more evenly distributes the SMP composite ring's recovery force and eliminates stress concentrations that existed in the fastener regions on the initial design.

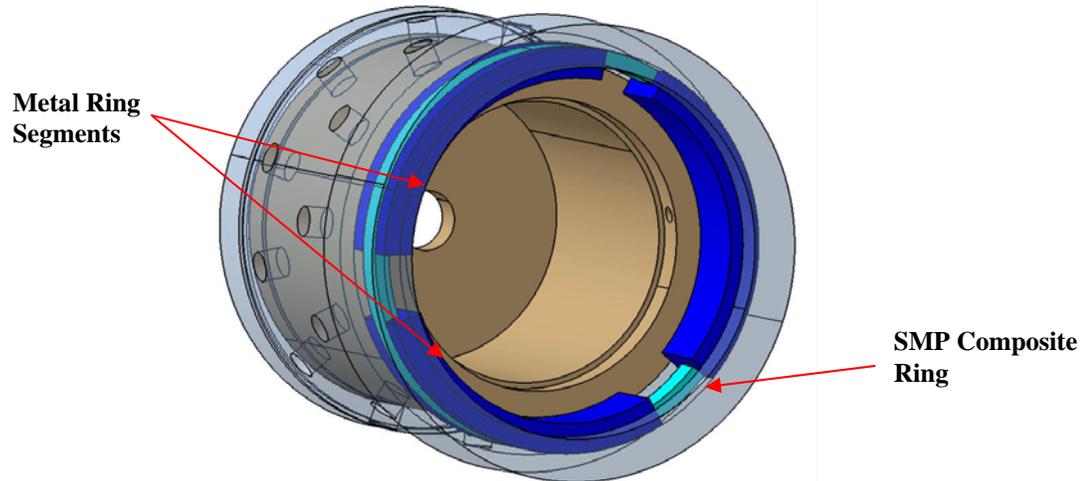


Figure 12. CRG's Phase II internal retaining ring design

CRG has successfully conducted initial functional testing of the redesigned venting mechanism to verify retraction of the SMP ring at the appropriate target temperature. Additionally, evaluations of the reinforced SMP material to determine available recovery force have been accomplished. CRG factored the results from these evaluations into the mechanism design as it evolved during Phase II efforts. A photo of the assembled retaining ring with an expanded, reinforced SMP retraction ring is presented in Figure 13. Two test motors were loaded with HTPB/AP-based propellant, assembled, and instrumented for slow cookoff testing.



Figure 13. SMP retaining ring assembly

In June 2009, the first rocket motor underwent slow cookoff testing in accordance with MIL-STD-2105 and STANAG 4382. When the test item reached the target temperature, the SMP composite ring retracted as designed, releasing the aft closure and providing additional venting area for the motor. At an approximate oven temperature of 400°F, the test item reacted. Initial engineering assessment categorized the result as an explosive reaction. Although the

venting mechanism functioned as designed, the additional vent area provided was insufficient to allow the motor to achieve a passing response. This result reinforces the conclusion that the effectiveness of a mitigation system is application dependent and is only part of an overall systems approach to IM technology integration.

## **MATERIALS OPTIMIZATION**

### **SMP formulations**

During Phase II, an in-house developed design model was used to obtain multiple cyanate ester-based SMP formulations having predicted  $T_g$ s in the target temperature range for the IM venting application. While the design model has been shown to predict  $T_g$  with a high degree of accuracy, it is generally used as a starting point in formulation efforts. Primary DMA testing of cyanate ester formulations was performed to determine the position and sharpness of the glass transition based on storage and loss modulus. For this application, a sharp transition is considered desirable. The selected formulation demonstrated the desired characteristics and has undergone secondary testing and further optimization.

Initial work on epoxy formulations has involved determining the upper  $T_g$  limit for epoxy SMP, based on using low-cost, commercially available starting materials. Commercially available monomers were surveyed and candidates were selected and procured based on their potential for increasing  $T_g$ . One promising approach currently under investigation has yielded a  $T_g$  approximately 30% higher than the baseline epoxy formulation. Further experiments are underway to determine the upper limit of  $T_g$  achievable with this approach, and to verify the shape memory characteristics of the resulting formulations.

### **Composite reinforcement**

Other material optimization efforts have included the identification of the high-strain reinforcement (HSR) material for the composite internal retaining ring. Resin compatibility issues and temperature stability concerns precluded the use of the HSR used in the Phase I effort. For Phase II, a high-temperature, HSR material developed by CRG under previous commercial and government projects is being used. This material will remain stable at resin cure and operational temperatures, and is compatible with cyanate ester and epoxy-based shape memory polymer systems.

## **SUMMARY AND CONCLUSIONS**

In a Phase I SBIR effort, CRG successfully demonstrated the internal SMP retaining ring as a venting system design at the prototype level. Benefits of the SMP venting system include the following:

- Ability to provide venting for slow cook-off situations
- Fail-safe nature (non-electronic activation)
- Ability to tailor across range of propellant autoignition temperatures
- Design simplicity
- Adaptability to many different solid rocket motor systems
- Applicability to munition containers

In Phase II, the internal ring design concept is undergoing prototype testing in an analog solid rocket motor representing an operational system. Testing includes slow cookoff testing in accordance with STANAG 4382. After successful completion of the Phase II slow cookoff testing program, this cookoff mitigation concept is expected to meet the requirements for a technology readiness level (TRL) of 5: validation of component or prototype in a relevant

environment. During the Phase II effort, a manufacturing plan to aid in the transition of the technology to Phase III will be generated.

### FUTURE EFFORTS

Phase II testing will conclude with a second full-scale slow cookoff test, with a pre-ignition element installed on the test motor's propellant grain in order to determine if igniting the motor in a controlled manner after activating the venting mechanism will produce an improved response.

Future efforts needed beyond Phase II to transition this technology to operational use and commercialize additional applications include the further characterization of SMPs tailored for specific IM applications, and the consideration of SMP-based venting devices for munition containers and warheads.

Another SMP-based IM mitigation concept under investigation involves the application of CRG's mature SMP fastener technology to munition container/canister venting. Success in this effort will result in the delivery of an improved container venting mechanism that increases safety of the munition or missile system without compromising effectiveness or reliability. Next-generation IM container venting systems relying on a thermally-activated SMP fastener interface will be capable of initiating container venting at the appropriate, tailored temperature, preventing dangerous pressure build-up in the container or canister while maintaining impact resistance.

In an Army-sponsored SBIR effort, CRG successfully developed an SMP-based fastening system that offers high-force hold and simple, quick attachment and detachment. CRG's rapid release fasteners hold more weight than commercially available detachable fastener systems and attach and detach with less force, when thermally activated. This system incorporates a unique, toughened SMP material that transitions from rigid to elastic during the fastening process. When the rapid-release system is activated, the fasteners become flexible, allowing simple, snap-on attachment. Figure 14 presents the basic operation cycle of the SMP fastener system.

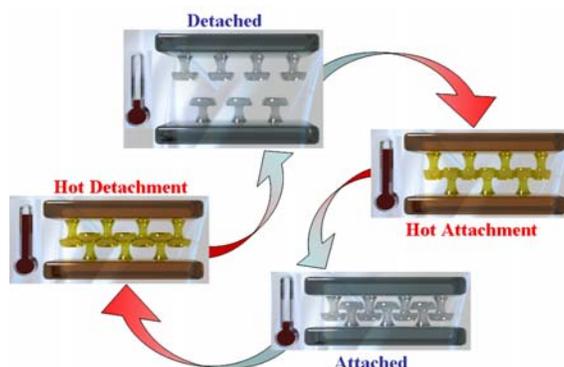


Figure 14. SMP fasteners' operation cycle

Once fastened, the system returns to a rigid state, locking the fasteners in place. The application of this SMP fastener system will create a robust, rapid-release fastening system for IM container vent/access panels. The fasteners' ability to change stiffness modulus and shape configuration under prescribed thermal stimulus, coupled with the high tensile and shear strength under normal operating conditions, makes them ideal for automatic venting applications that do not compromise the integrity of munition containers.