# Heat-Storage Modules Containing LiNO$_3\cdot$3H$_2$O and Graphite Foam

**Heat capacity per unit volume has been increased.**

*NASA's Jet Propulsion Laboratory, Pasadena, California*

A heat-storage module based on a commercial open-cell graphite foam (Poco-Foam or equivalent) imbued with lithium nitrate trihydrate (LiNO$_3\cdot$3H$_2$O) has been developed as a prototype of other such modules for use as short-term heat sources or heat sinks in the temperature range of approximately 28 to 30 °C. In this module, the LiNO$_3\cdot$3H$_2$O serves as a phase-change heat-storage material and the graphite foam as thermally conductive filler for transferring heat to or from the phase-change material. In comparison with typical prior heat-storage modules in which paraffins are the phase-change materials and aluminum fins are the thermally conductive fillers, this module has more than twice the heat-storage capacity per unit volume.

The use of LiNO$_3\cdot$3H$_2$O as a phase-change heat-storage material is not new in itself, but heretofore, it has been used with aluminum fins. Open-cell graphite foam has been used as the thermally conductive filler material in conjunction with paraffin phase-change materials in some prior heat-storage modules but, heretofore, it has not been used with LiNO$_3\cdot$3H$_2$O because graphite foam is hydrophobic and, therefore not readily wet by LiNO$_3\cdot$3H$_2$O. The novelty of the present development lies in the choice of materials to make it possible to use graphite foam as the filler with



The **Components Shown Separately** here were assembled to make a heat-storage module. Prior to sealing the module, the open-cell graphite foam was filled with molten LiNO$_3\cdot$3H$_2$O containing small proportions of a surfactant and a freezing catalyst.

LiNO$_3\cdot$3H$_2$O in order to exploit the greater (relative to aluminum) specific thermal conductivity of graphite to reduce the mass of filler needed to obtain a given level of thermal performance.

The prototype heat-storage module consists of an LiNO$_3\cdot$3H$_2$O-imbued open-cell graphite foam core of 76-percent porosity in an aluminum housing that has a ribbed top that provides a rigid mounting surface for electronics. During fabrication, grooves to receive the ribs were cut into the open-cell graphite foam core (see figure). To overcome the hydrophobicity of the graphite foam to enable the core to absorb the LiNO$_3\cdot$3H$_2$O, an organosilicon surfactant was added to the molten

LiNO$_3\cdot$3H$_2$O in the proportion of 0.3 mass percent.

Also added to the LiNO$_3\cdot$3H$_2$O was 1 mass percent of zinc nitrate, which serves as a freezing catalyst to reduce, to an interval of 2 C°, what would otherwise be the susceptibility of LiNO$_3\cdot$3H$_2$O to freezing supercooling by as much as 35 C°. With this catalyst, the LiNO$_3\cdot$3H$_2$O freezes at 28 °C when cooled from a higher temperature and melts at 30 °C when warmed from a lower temperature.

*This work was done by Michael Pauken and Nickolas Emis of Caltech and John Bootle of XC Associates for NASA's Jet Propulsion Laboratory. For more information, contact iaoffice@jpl.nasa.gov.*
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# Precipitation-Strengthened, High-Temperature, High-Force Shape Memory Alloys

**Shape memory alloys capable of performing up to 400 °C have been developed for use in solid-state actuator systems.**

*John H. Glenn Research Center, Cleveland, Ohio*

Shape memory alloys (SMAs) are an enabling component in the development of compact, lightweight, durable, high-force actuation systems particularly

for use where hydraulics or electrical motors are not practical. However, commercial shape memory alloys based on NiTi are only suitable for applications

near room temperature, due to their relatively low transformation temperatures, while many potential applications require higher temperature capability.

Consequently, a family of $(Ni,Pt)_{1-x}Ti_x$ shape memory alloys with Ti concentrations $x \leq 50$ atomic percent and Pt contents ranging from about 15 to 25 at.% have been developed for applications in which there are requirements for SMA actuators to exert high forces at operating temperatures higher than those of conventional binary NiTi SMAs. These alloys can be heat treated in the range of 500 °C to produce a series of fine precipitate phases that increase the strength of alloy while maintaining a high transformation temperature, even in Ti-lean compositions.

The absolute minimum requirement for determining the operating temperature of an SMA is the temperature of the martensite-to-austenite, solid-state phase transformation, which is the source of the shape memory behavior. However, the present high-temperature, high-force SMAs can be used at temperatures up to 400 °C not only because they exhibit a range of high transformation temperatures, but because these materials also exhibit high strength (resistance to dislocation mediated deformation processes) in both the austenite and martensite phases, have a relatively high recovery temperature, and also exhibit excellent dimensional stability (little or no irrecoverable strain component during the transformation process). Consequently, these alloys are attractive for use in performing actuator and control functions particularly in the aggressive environments often encountered in aerospace, automotive, and down-hole energy exploration applications.

The composition of an alloy of this type is given generally by the empirical formula $Ni_{x-y-z}Pt_yM_zTi_{100-x}$, where M can be Au, Pd, or Cu; $x$, $y$, and $z$ are atomic percentages; $50 \leq x \leq 55$; $10 \leq y \leq 30$; $0 \leq z \leq 10$. These alloys are precipitation-hardenable, but unlike in prior Ti-rich NiTi alloys, the slightly Ti-lean composition prevents the formation of the $Ti_2Ni$ phase, which is a coarse globular phase that cannot be thermally tailored in as much as it appears during solidification. Instead, one can rely on precipitation of fine $(Ni,Pt)_3Ti_2$ structures and other intermetallic phases for enhanced performance. These precipitates are often lath-like in structure and, in many cases, submicron in size. The precipitate volume fraction can also be tailored through heat treatment and alloy composition. These precipitates result in additional strengthening of the austenite (high-temperature) matrix phase and increase the resistance of the martensite phase against slip, without exerting a significant effect on the detwinning stress. Thus, the overall effects are greater specific work output with better dimensional stability, and superior mechanical properties, especially at high temperatures.

The desirable properties of these alloys include the following:
- Their transformation temperatures variously remain stable or increase with aging time.
- They exhibit specific-work-output levels >9 $J/cm^3$ and good work performance, comparable to those of conventional binary NiTi alloys.
- Unlike NiTi and other NiTi-based ternary SMAs, these alloys do not exhibit transformation temperatures lower than those of corresponding stoichiometric alloys; indeed, these alloys exhibit transformation temperatures higher than those of similar alloys that have Ti-rich compositions.
- Unlike in the prior NiTi-based ternary SMA alloys, which exhibit decreases in transformation temperatures with increased aging time or thermal cycling, these alloys exhibit stabilization of, or increases in, transformation temperatures with aging.
- These alloys can be processed into such bulk forms as bar, rod, sheet, plate, and wire through conventional thermomechanical processes. Because these alloys have high recrystallization temperatures (700 to 800 °C), they are amenable to heat treatment and aging after thermomechanical processing, without adversely affecting grain sizes.
- The high recrystallization temperatures also make these alloys suitable for use in applications in which they could be subjected to significant heating above their rated temperatures.