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Richard D. Kopa
September 1979

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EFFICIENCY OF ENERGY CONVERSION
IN NITINOL

by
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ABSTRACT

Nitinol—one of several Shape Memory Effect (SME) alloys—is known to be a suitable medium for the conversion of heat to usable mechanical work in a "solid state" heat engine. In the present study, the efficiency of the energy conversion in Nitinol is investigated experimentally.

An electronically controlled Cycle Simulator subjects a single Nitinol wire element to the stress-strain-temperature cycles corresponding to a specific thermodynamic cycle (e.g., constant-strain isothermal, stress-limited isothermal, constant-stress isothermal, semi-adiabatic, etc.), as selected during the investigation. The test parameters, which are varied singly or in combination, include various stress levels, stress rates, percent of elongation of the wire, temperature levels, heating and cooling rates, cycling speeds, etc. Efficiency values as a function of these variables are plotted in graphs and the factors affecting efficiency are discussed. The highest thermodynamic efficiency thus far determined is 1.2 percent (approximately 6 percent of Carnot efficiency), with a concomitant Nitinol wire life expectancy on the order of $10^4$ cycles. However, these values are not regarded as the highest attainable. It is anticipated that higher efficiency as well as life expectancy would be realized with Nitinol alloys perfected through basic materials research and development. Nevertheless, the fundamental limitation of the energy conversion efficiency is set by the inefficient type of thermodynamic cycle—namely, the isothermal cycle—to which the "solid
state" heat engine operation (with presently available SME materials, such as Nitinol) is restricted. The reasons for this restriction are discussed in Chapters 5 and 6.

The simple constant-strain isothermal cycle is analyzed and described in stress-strain coordinates and in a T-S diagram. An analytic expression for the calculation of the energy conversion efficiency is presented, along with experimental investigation of the proposed postulates. A few preliminary investigations of various approaches to efficiency improvement are reported, and one promising research area is suggested.

Further basic and materials research is needed for better understanding of the energy conversion process in Nitinol, for the clarification of the extent of the validity of the proposed postulates, and for the determination of a rigorous expression for the efficiency of the constant-stress isothermal cycle.
1. INTRODUCTION

Devices and heat engines which employ Shape Memory Effect alloys (e.g., Nitinol) as the energy conversion media have been described in the literature [1]. Since these engines are capable of working at nearly ambient temperatures and at a relatively small temperature difference between the hot and cold reservoir, they appear particularly suitable to applications involving solar flat plate collectors, geothermal and industrial waste heat sources, or for bottoming cycles of conventional power plants. Suggested commercial applications include solar cooling of buildings, agricultural pumping, decentralized solar power generation, etc. However, thus far only information on the theoretically estimated efficiencies, and some fragmentary information on experimentally determined efficiencies of these devices, has been published.

This paper describes an experimental parametric study of a Nitinol alloy subjected to a number of simulated thermodynamic engine cycles, in which the test parameters are systematically varied in such a way that efficiency values as a function of these parameters are obtained, and the most efficient type of thermodynamic cycle is identified.

The information derived can serve as a basis for the design of a "solid state" heat engine with the highest attainable efficiency and/or power density, for the comparison of theoretical and experimental efficiencies, as well as to provide reference data for further research and development of thermoelastic materials.
Another objective of the study is the determination of an engine cycle which offers the lowest progressive degradation, irreversible damage and creep, and therefore the longest life of the investigated thermoelastic material, which in this study is used in the form of wire elements subjected to cyclic tension stress.

2. BACKGROUND

The Shape Memory Effect (SME) in alloys has been extensively treated in the literature and therefore will not be discussed here. For familiarization with the subject, Reference [2], and for more in-depth study, References [3, 4, 5 and 6] are suggested. Among the alloys exhibiting SME, Nitinol has been most widely studied and used in various technical applications. Reference [2] presents a comprehensive overview and an extensive literature survey of research activity on Nitinol.

More recently, the efficiency of the energy conversion in SME alloys has been the subject of theoretical study by several investigators. In Reference [7] thermodynamic efficiency of 4.9 percent has been predicted, and in References [8], [9], [10] and [11] efficiencies in the range of 10 percent to over 20 percent have been calculated. Moreover, some limited information on experimentally determined energy conversion efficiencies in Nitinol has been reported in Reference [2], ranging from 10 percent to 16 percent, and in Reference [12], amounting to 2.7 percent. It should be noted that these studies were based on considerably differing assumptions and/or experimental
conditions as well as on SME alloys of substantially different properties.

In the previous study at this Laboratory [12], the thermodynamic efficiency of the energy conversion process in Nitinol was investigated, with particular interest in determining the repeatability of the results over a large number of work cycles. It was estimated that for economically feasible technological applications, the life of the SME alloy, before failure due to fatigue, should extend to over $10^6$ cycles.

3. EXPERIMENTAL SYSTEM AND METHOD

Briefly, the conversion process of heat to mechanical work during the Nitinol engine cycle involves the following steps:

1) The Nitinol wire is cooled by submerging it into the cold bath to a temperature which is well below its transformation temperature, and consequently its crystalline structure stabilizes in a martensitic phase.

2) While in the cold bath, it is easily stretched (Nitinol in the martensitic phase is highly ductile) by applying a moderate external force and elongated to a predetermined length (typically 1.0 percent to 5.0 percent strain).

3) Thereupon the wire—while still elongated—is heated by submerging it into the hot bath, where it develops high stress (as the result of the reversed martensitic phase transformation process).
4) Overcoming applied external load, the Nitinol wire contracts with a great force until it attains its original length. During the contraction, useful mechanical work $W$ is produced by the wire which is equivalent to the product of the force $F$ times the linear change $AL$ of the wire length during the contraction ($W = FL$).

At the completion of the wire contraction, a stabilized crystalline structure of the high temperature phase (austenitic) is again attained. The Nitinol is now ready for the next cycle which starts with the cooling of the wire element.

To facilitate an accurate and repeatable execution of the above cycle, at various parametric conditions, an electronically controlled Cycle Simulator was designed.

The major components of the test apparatus are schematically presented in Figure 1. A test sample of Nitinol wire $N$ is stretched between arm $A_1$, axially sliding on a rotating shaft, and arm $A_2$, solidly attached to the same shaft. Arm $A_2$ carries a flexible beam on which is cemented strain gage $S$, measuring the force exerted by the Nitinol wire $N$. The axial motion of arm $A_1$ is effected by a lead screw $L$ which is driven by servomotor $M_1$. The position of the arm $A_1$ in respect to arm $A_2$ is transmitted by means of a potentiometer readout $R$ to the oscilloscope OS as a horizontal deflection of the electron beam. The vertical deflection of the beam is effected by an amplified signal from the strain gage $S$. The stress-strain diagram displayed on the oscilloscope screen is recorded by means of a video camera and stored on a video tape.
The transfer of the Nitinol wire $N$ back and forth from the hot reservoir $H$ and cold reservoir $C$ is effected by a $300^\circ$ rotation of the shaft which is driven by the servomotor $M_2$. The clockwise and counterclockwise rotation of the shaft as well as of the lead screw $L$ is electronically controlled by two linear servoamplifiers in the electronic control system $EC$. The sequence of events, of positions, and of the speed of motion is programmable to permit simulation of a desired type of the thermodynamic engine cycle.

The actual design drawing of the mechanical part of the apparatus is shown in Figure 2, and the complete experimental setup is shown in Figure 3.

Since all known Nitinol engines operate on the (constant-strain, stress-limited, or constant-stress) isothermal cycle, this type of thermodynamic cycle was selected for the first series of experiments. The isothermal cycle consists of stretching an SME wire element in a cold bath under constant low temperature (isothermally), and thereupon transferring the stretched wire into a hot bath where it contracts, while developing strong force, under constant elevated temperature (isothermally). Typical isothermal work cycles (presented in Figure 4 through Figure 7) are discussed below:

Figure 4 is a sample of a video record of a constant-strain isothermal cycle with the pertinent parametric information (e.g., cycle No. 1554, Nitinol wire No. 1, length of wire 21.8 in, diameter of wire 0.019 in, temperature of cold reservoir $+2.3^\circ$C and of hot reservoir $+56.3^\circ$C, elongation $\Delta L = 0.29$ in, and type of cycle ISOTHERMAL).
The horizontal line at the bottom represents stretching of the wire (from left to right), under constant temperature; the vertical line represents the rise in stress after transfer of the wire into the hot bath, and the sloping line from right to left represents the contraction of the wire in the hot bath (at constant temperature). The area enclosed by these lines represents the effective work or mechanical energy produced by the wire element during one cycle.

In the following series of tests, the Nitinol wire was heated by an electric pulse, instead of submerging it in a hot bath. The resulting record taken by a Polaroid camera from the oscilloscope screen is shown in Figure 5.

The intensity and duration of the electric pulse (24V, 9A, 350 ms) in Figure 5 was adjusted so as to produce the same peak stress as in Figure 4. By this procedure, a correlation can be established between the temperature of the hot bath and the heat input to the wire during the phase transformation which generates the peak stress.* The peak stresses in this series of tests ranged from 30Kpsi to 50Kpsi. The elongation (strain) of the wire ranged from 1.3 percent to 1.8 percent.

A noticeable difference exists between the horizontal lines of the records in both Figures. In Figure 4 the perfectly horizontal line signifies complete absence of stress during the stretching of the wire. This was attained by subjecting the virgin wire to 1000 training cycles of heating and cooling with a progressive change of the strain. (Training of Nitinol wires was extensively investigated

*See the Appendix
by Johnson [13].) By this treatment, a "second memory" effect
developed in the wire which consequently caused an elongation of the
wire automatically upon submerging it into the cold bath. In Figure 5
the training did not produce so perfect a result and only a part of
the elongation is stress-free.

In another series of tests, a "stress-limited" cycle was
investigated. Figure 6 presents a typical result. The Nitinol wire,
in this case, was suspended on a preloaded compression spring attached
to the sliding arm A₁ (Figure 1). As indicated on the record, a
lower peak stress at higher elongation (2.7 percent) resulted. The
durability of the wire element subjected to this type of cycle is
presently under investigation. This cycle is an intermediate type
between the constant-strain isothermal and the constant-stress
isothermal cycle.

A typical record of a constant-stress isothermal cycle is shown in
Figure 7. The lower horizontal line and its extension sloping upwards
(from left to right) represents the isothermal stretching of the
Nitinol wire at constant temperature in the cold bath. The following
short vertical line results when the strained wire is transferred into
the hot bath. The upper horizontal line represents the contraction of
the Nitinol wire (power stroke) at constant temperature and constant
stress (in the hot bath). The following steeply sloping line in a
downwards direction represents the drop of stress at the end of the
wire contraction (end of power stroke).
To execute this cycle, it was necessary to slightly modify the Cycle Simulator apparatus by attaching one end of the Nitinol wire to a cable (guided over three pulleys) which transmits a constant force exerted by suspended calibrated weights.

In these tests, the Nitinol wire was initially stretched in the cold bath (2°C) to 8 percent strain, then transferred into the hot bath (80°C) where the wire contracted under constant stress of 37Kpsi (26.0Kg/mm²), lifting a weight of 4.78Kg. After several cycles, the load was reduced to produce 29Kpsi and the cycle was repeated about 200 times. A stabilized work diagram similar to that shown in Figure 7 was then recorded in all successive cycles. The permanent (irreversible) wire elongation amounted to approximately 3 percent of the original strain (portion of the lower horizontal line extending to the left and outside of the area enclosed by stress-strain lines), and the remaining 5 percent constituted the effective periodic strain of the "stabilized" cycles.

4. EXPERIMENTAL RESULTS

The efficiency \( \eta \) of the conversion of heat to mechanical work is defined as the ratio of the useful work \( W \) produced by the Nitinol wire, and of the heat input \( Q \) to the wire element during every engine cycle.

\[
\eta = \frac{W}{Q} \quad (1)
\]
The mechanical work is determined by the planimetry of the work diagram (area on the oscilloscope screen enclosed by the stress-strain lines). The heat input was calculated on the basis of experimental data presented in Reference 2, or directly measured when the heat to the wire was supplied by an electric pulse (see the Appendix).

Equation (1) can be written as follows:

\[ n = \frac{FEaL[g]/L}{Q[g]} 0.981 \]  \hspace{1cm} (2)

where \( E \) is the force in Kg exerted by the wire at the peak stress, \( \varepsilon \) is elongation of the wire in mm, \( Q[g] \) is the total heat input per cycle in Joules per gram of wire element, \( a \) is the work diagram area factor, \( L[g]/L \) is the ratio of the length of wire weighing 1.0 gram to the length of the test wire (for Nitinol wire of \( D = 0.919 \) in = 0.483 mm, the length \( L[g] = 846 \) mm).

For a constant-strain isothermal cycle \( \alpha = 0.5 \), and for the theoretically ideal cycle \( \alpha \) would approach unity.

Equation (2) can further be written as follows:

\[ n = \frac{\sigma_3 \varepsilon a/\gamma}{Q[g]} 0.249 \]  \hspace{1cm} (3)

where \( \sigma_3 \) is the maximum peak stress in Kpsi, \( \varepsilon \) is strain in percent of elongation, \( \gamma = 0.234 \) lb/in\(^3\) is the density of Nitinol, and 0.249 is a conversion factor.

Equation (3) is graphically represented in Figure 8a for a typical value of the heat input to the wire element \( Q = 50 \) Joule/g (for full
martensitic transformation) and $\alpha = 0.5$, corresponding to a typical constant-strain isothermal cycle. Similarly, Figure 8b presents the plot of Equation (3) for $\alpha = 1.0$, which would apply to an ideal engine cycle.

Examination of Figure 8 indicates that the theoretically predicted efficiencies in References [8] to [11] of 10 percent and above are not attainable in any type of thermodynamic cycle involving heat input of the order of 50 Joules (or more) per gram of the SME material. For example, to obtain efficiency of 10 percent with an ideal engine cycle ($\alpha = 1.0$), the Nitinol wire would have to develop a recovery stress over 80Kpsi at 6 percent of elongation. However, no presently known SME alloy would sustain cyclic (heat-stress-strain) loads at this stress level for more than a few cycles. Even at considerably lower stress and elongation levels, the Nitinol wire element would fail after a few cycles because of cumulative permanent deformation and irreversible damage due to progressive creep.

The typical test results which were obtained in this study are presented in the following figures. The SME material used in all tests was Nitinol wire of diameter $D = 0.019$ in., 50.4 percent atomic Ni, produced by TIMET. The individual types of engine cycle investigated are identified as follows:

(A) Symbol O, represents isothermal constant-stress cycle ($\varepsilon = 5.0$ percent) at constant $T_3 = 75^\circ$C, with variation of $\sigma_3$ from 17.7 to 37.1Kpsi.
Symbol \( \triangledown \), represents isothermal constant-strain cycle 
\((\varepsilon = 1.3 \text{ percent})\) with variation of \( I_3 \) from 45°C to 70.4°C.

Symbol \( \circ \), represents isothermal constant-strain cycle 
\((\varepsilon = 0.5 \text{ percent})\) with variation of \( I_3 \) from 34°C to 84°C.

Symbol \( \diamond \), represents isothermal stress-limited cycle 
\((\varepsilon = 0.5 \text{ percent})\) with variation of \( I_3 \) from 37°C to 70°C.

Symbol \( \Box \), represents isothermal constant-strain cycle, 
strain varied in steps: \( \varepsilon = 0.5 \text{ percent}, \varepsilon = 1.1 \text{ percent} \) and \( \varepsilon = 1.6 \text{ percent} \), at constant \( I_3 = 51°C \).

Symbol \( \odot \), represents isothermal constant-strain cycle, 
strain varied in steps: \( \varepsilon = 0.5 \text{ percent}, \varepsilon = 1.1 \text{ percent} \) and \( \varepsilon = 1.6 \text{ percent} \), at constant \( I_3 = 71°C \).

Symbol \( \Delta \), represents isothermal constant-stress cycle 
\((\varepsilon = 5.0 \text{ percent})\) and constant peak stress \( \sigma_3 = 37.1\text{kpsi} \), 
with variation of \( I_3 \) in steps: 53°C, 61°C and 77°C.

Every data point in Figures 9 through 15 represents, on the average, 
several hundreds and every curve several thousands of repeated test 
cycles. Every series of tests has been started with a new trained and 
stabilized wire after at least 500 repeated cycles.

Figure 9 represents the recovery peak stress, resulting during 
various types of the isothermal engine cycle, as the function of the 
hot reservoir temperature \( I_3 \). The temperature of the cold reservoir 
\( I_1 \), was maintained for all tests between +1°C and +2°C, except for 
the stress-limited cycles (curve \( \Box \)), for which it was +25°C.
The examination of Figure 9 reveals the following:

a) Generally, the peak recovery stresses appear to be substantially higher than the recovery stresses reported in the literature (e.g., Reference [14]). However, the peak recovery stresses of the test series \( B, C, E, \) and \( F \), for the same \( \varepsilon \) are noticeably different. This could be due to the nonidentical thermal and mechanical history (resulting during manufacture, "training" period and the test period) of the individual Nitinol wire elements. For example, in test series \( B \) the strain \( \varepsilon = 1.3 \) percent was kept constant, but in \( E \) and \( F \) it was varied from \( \varepsilon = 0.5 \) percent to \( \varepsilon = 1.6 \) percent.

b) The peak recovery stresses of the stress-limited cycles (curve \( D \)) are substantially higher than the recovery stresses of the constant-strain cycles (curve \( C \)), although the strain \( \varepsilon = 0.5 \) percent was maintained the same for both test series. This effect resulted when the temperature \( T_1 \) of the cold reservoir for the stress-limited cycles was raised to \( +25^\circ \)C. In such case the phase transformation process is incomplete. Only a part of the austenitic phase is transformed during the cooling of the Nitinol wire to thermal martensite, while another part is contributed by the stress-induced martensite during the wire straining. Because of the substantial stress \( \sigma_2 \) at the end of straining, a correspondingly higher peak recovery stress \( \sigma_3 \) results. Therefore, for \( T_1 = +25^\circ \)C, the stress-limited operation was necessary to prevent excessively high peak recovery stresses, which otherwise would rapidly degrade the wire element.
Figure 10 presents the useful work \( W \) produced by the various types of engine cycles as the function of the peak recovery stress \( \sigma_3 \). Generally, the useful work increases linearly with the peak recovery stress. The yield is highest for the constant-stress cycle (curve \( \text{A} \)), and is more than three times as high when compared to the constant-strain cycle (curve \( \text{B} \)) at the same peak stress level.

In contrast to this, the stress-limited cycle \( \text{D} \) produces lower useful work \( W \) than the constant-strain cycle \( \text{C} \) when both cycles are performed at the same strain (e.g., \( \epsilon = 0.5 \) percent). This may be explained by the fact that a substantial amount of work has to be expended for straining of the wire in the cold reservoir at \( T_1 = 25^\circ \text{C} \), because at this temperature, the Nitinol has been only partially transformed to the martensitic phase.

Figure 11 presents the thermodynamic efficiency \( \eta \) of the conversion of heat to mechanical work in Nitinol as the function of the hot reservoir temperature \( T_3 \). For the determination of \( \eta \), the heat input to the wire element must be known (see Equation (1)). For the test series \( \text{G} \) and \( \text{B} \) (broken lines), the heat input \( Q_H \) was calculated as follows: to the value of the latent heat of transformation \( \Delta H = 5.78 \text{ cal/g} \) was added the sensible heat \( C_p(T_3 - T_1) \), where \( C_p = 0.11 \text{ cal/g deg} \) (data taken from Reference [27]). This represents only a first order rough approximation to the actual heat input, as will be shown later. For the test series \( \text{C}, \text{D}, \text{E} \) and \( \text{F} - \text{E} \), \( \text{F} \) are plotted in Figure 13—the heat input was measured by the electric pulse method (see the Appendix). Thus far no reliable
method has been developed for the measurement of the heat input $Q_H$ to the wire element during the constant-stress isothermal cycle. The electric pulse method cannot be applied because at high strains (as employed in constant-stress cycles, e.g., $\varepsilon = 5.0$ percent) the contraction of the wire element during the shape recovery cannot be effected fast enough, and therefore the heat losses from the wire element to the surroundings would introduce a significant error. For the test series (6) the heat input $Q_H$ was estimated assuming for the constant-stress cycles the same relative difference between the calculated and measured values of $Q_H$ as was experimentally determined for the constant-strain cycles.

The highest efficiency was obtained for most of the test-cycles at hot reservoir temperature $T_3 = 60^\circ$C, and for the series (D) at about $T_3 = 55^\circ$C. The effect of this shift (of the efficiency maximum toward the lower temperature $T_3$) on the ratio of the engine cycle efficiency $\eta$ to the Carnot efficiency $\eta_C$ is illustrated in Figure 12. Particularly pronounced effect is evident for the stress-limited cycle series (D), where it is the consequence of the smallest temperature difference $\Delta T = T_3 - T_1$ between the hot and cold reservoir. From Figure 12 it can be inferred that by a proper selection of the temperature $T_1$, $T_3$ and of the maximum stress level $\sigma_3$ a stress-limited or a constant-stress isothermal cycle can be found with a substantially higher $\eta/\eta_C$ ratio than shown. Such a cycle would make the Nitinol heat engine more competitive with other
energy conversion devices where heat sources with small temperature difference between the hot and cold reservoir (e.g., $\Delta T \leq 20^\circ C$) are available.

Figure 13 shows the thermodynamic efficiency as the function of heat input $Q_H$ to the wire element for various types of engine cycles. The superiority of the constant-stress cycle $A$ and $G$ is apparent.

Figure 14 presents the thermodynamic efficiency as the function of the peak recovery stress and points out the advantage of the constant-stress cycle $A$ over the constant-strain cycle $C$. If, for example, the requirement of the wire durability should dictate the peak recovery stress limit at 25Kpsi, the efficiency of the constant-stress cycle would be almost three times higher than that of the constant-strain cycle.

Indeed, the experimental results obtained to date indicate that for continuous cycling without noticeable progressive elongation of the Nitinol wire element, the maximum permissible recovery stress should not exceed 25Kpsi (17.6 Kg/mm$^2$). This limits the strain (for the tested material) to about 1.0 percent for the constant-strain isothermal cycle, and to about 5.0 percent for the constant-stress isothermal cycle. At this writing, all tests were repeated for less than $10^4$ cycles and the durability as well as the cumulative permanent elongation of the wire element due to creep have not been determined beyond that limit.
Nevertheless, in the case where a perfect "second memory" was established in the trained wire element (see Figure 4), no detectable cumulative permanent elongation was observed even after several thousand cycles.

Only a small part of the planned research program has been completed thus far, and therefore the measured efficiency values reported should not be regarded as the highest attainable. Some improvement of energy conversion efficiency may be possible by thermal and mechanical pretreatment and by alloying of Nitinol with another metal.

However, on the basis of results obtained to date, it is clearly evident that a substantial improvement of the energy conversion efficiency could be attained only if the required heat input $Q_H$ to the Nitinol wire during the engine cycle could be substantially reduced.

5. ANALYSIS OF THE ISOTHERMAL CYCLE

The isothermal Nitinol heat engine cycle can be described in a stress-strain diagram, and the flowpath of energy through the cycle can be defined in the corresponding temperature-entropy diagram. Figure 15a presents a simple constant-strain isothermal cycle in the stress-strain coordinates. The cycle starts at point 1 with straining of the Nitinol wire in the cold bath (along the isotherm $I_1$) until the point 2. Then the wire is transferred into the hot bath and heated (under constant strain $\varepsilon_2$) until it attains the temperature
I_3 (while developing high recovery stress) at point 3. Thereupon it is allowed to contract at constant temperature I_3 performing useful work and returning to the initial strain e_1 at point 4. Note that point 4 does not lie on the isotherm I_3 (as theoretically would be expected for an ideal SME material), but on or near the isotherm I_1. This drop in stress is due to non-ideal thermodynamic behaviour of Nitinol, and the resulting magnitude of irreversible losses is dependent on the type of cycle used. It is well known that the change of the thermodynamic state of Nitinol (and other SME materials) from one point to another in the stress-strain-temperature space continuum depends on the path by which the new state has been reached. This means that the new state depends on the previous thermal and mechanical history, and consequently the initial state may not necessarily be attained by a reversed change of the state parameters. Therefore, the thermodynamic state parameters ($\sigma$, $\epsilon$, $T$, $U$, $H$, $S$) are not uniquely definable in terms of specific thermodynamic functions.

A hypothetical "entropy diagram" is schematically shown in Figure 15b. The cycle is defined again by the isotherms I_1 and I_3 and by the lines of constant strain e_1 and e_2. Starting the cycle at point 1 by straining the wire the exothermic heat of elastic deformation $Q_0$ generated in the Nitinol wire, during the straining (because the coefficient of linear thermal expansion of Nitinol in the transition region is negative [15]) is rejected to the cold reservoir (point 1 to point 2). Therefore, the entropy of the Nitinol wire during isothermal straining decreases; this means that in the entropy
diagram point 2 must lie to the left of point 1. Conversely, during the wire contraction (point 3 to point 4) the endothermic heat of elastic recovery $Q_R$ is absorbed by the wire from the surroundings (i.e., isothermic contraction in the hot bath), and the entropy increases (point 4 lies to the right of point 3, as shown in Figure 15b).

For isothermal elastic deformation [16,17] (of completely martensitic Nitinol) the heat $Q_D$ can be expressed as:

$$Q_D = (\alpha_2 - \alpha_1) T_1 \frac{\alpha_T}{\gamma}$$

In this equation, $\alpha_T$ is the negative coefficient of linear thermal expansion $[(^oC)^{-1}]$ in transition region, $T_1$ is the absolute temperature of the cold reservoir, $(\alpha_2 - \alpha_1)$ is the isothermal change in stress during straining [kg/m$^2$], $\gamma$ is the density of Nitinol [kg/m$^3$] and $J$ is the mechanical equivalent of heat [427.8 mkg/kcal].

During the heating of the wire in the hot bath (from point 2 to point 3) the heat $Q_H$ is absorbed by the Nitinol wire:

$$Q_H = C_p(T_3 - T_1) + \Delta H_{M \rightarrow A}^{(\sigma)}$$

where $C_p$ is specific heat of Nitinol [0.11 kcal/kg] (nearly constant in the range considered), and $\Delta H_{M \rightarrow A}^{(\sigma)}$ is the latent heat of phase transformation (Martensite $\rightarrow$ Austenite) in the prestrained wire while the recovery stress rises from $\sigma_2$ to $\sigma_3$ ($\Delta H_{M \rightarrow A}^{(\sigma)}$ to be determined experimentally).
In Figure 15b this change is schematically represented by a straight line connecting points 2 and 3. In reality, this would be an integral curve indicating the progressive entropy increase of the Nitinol during the reverse phase transformation, as the wire element is heated from I₁ to I₃. Moreover, during the cooling of the wire in the cold bath (point 4 to point 1) the progressive decrease in entropy would in reality be indicated by a similar curve of a reverse trend.

During the wire contraction (point 3 to point 4) the endothermic heat of shape recovery \( Q_R \) is absorbed by the Nitinol (assuming no phase transformation occurs during the contraction):

\[
Q_R = (\sigma_3 - \sigma_4)T_3 \frac{\alpha_I}{\gamma J} \tag{6}
\]

where \( \sigma_3 - \sigma_4 \) is the isothermal change in stress during the shape recovery (point 3 to point 4).

Finally, during cooling of the wire in the cold bath (point 4 to point 1) the heat \( Q_C \) is rejected:

\[
Q_C = C_p (T_3 - T_1) + \Delta H^{A \rightarrow M}_{(o)} \tag{7}
\]

where \( \Delta H^{A \rightarrow M}_{(o)} \) (to be determined experimentally) is the latent heat of transformation of austenite to martensite in relaxed Nitinol wire (zero external force).

Note that \( \Delta H^{M \rightarrow A}_{(o)} \) and \( \Delta H^{A \rightarrow M}_{(o)} \) are not equal; the Lechatelier principle demands that \( \Delta H^{M \rightarrow A}_{(o)} > \Delta H^{A \rightarrow M}_{(o)} \). Their difference is:
\[ \Delta h = \Delta h^{M\to A} - \Delta h^{A\to M} = Q_H - Q_C \]  

Similarly, \( Q_R \) and \( Q_D \) are not equal and their difference is:

\[ \Delta r = Q_R - Q_D \]

The sum

\[ \Delta q = \Delta h + \Delta r = W \]

represents the total amount of heat which theoretically could be converted into mechanical work during the isothermal cycle. The major part of the total heat, namely the sensible heat \( C_p (T_3 - T_1) \) and the latent heat of phase transformation at zero external force \( \Delta h^{A\to M} \) (and the heat of elastic deformation \( Q_O \)), is wasted—i.e., is transferred from the hot to the cold reservoir.

The theoretical energy conversion efficiency of any type of thermodynamic cycle can be expressed as:

\[ n = \frac{W}{Q} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} \]  

where \( Q_{in} \) is the total heat absorbed by the SME wire element in the hot reservoir, and \( Q_{out} \) is the heat rejected from the wire to the cold reservoir. For the constant-strain isothermal cycle employing SME material this becomes:
\[ n = 1 - \frac{Q_C + Q_D}{Q_H + Q_R} \]  \hspace{1cm} (12)

Substituting Eqs. (4), (5), (6) and (7) in (12) yields for the efficiency of the constant-strain isothermal cycle:

\[ n = 1 - \frac{C_p(T_3 - T_1) + \Delta H^A_{(T)} + (\sigma_2 - \sigma_1)T_1 \frac{\alpha_T}{\gamma}}{C_p(T_3 - T_1) + \Delta H^M_{(T)} + (\sigma_3 - \sigma_4)T_3 \frac{\alpha_T}{\gamma}} \]  \hspace{1cm} (13)

or substituting Eqs. (8) and (9) in (12) gives:

\[ n = \frac{\Delta h + \Delta r}{Q_H + Q_R} = \frac{\Delta q}{Q_H + Q_R} \]  \hspace{1cm} (14)

It is proposed that the theoretical limit of the efficiency of energy conversion in Nitinol subjected to a constant-strain isothermal cycle is given by Equation (14).

From Equation (13) it is evident that the efficiency \(n\) will increase with increasing peak recovery stress \(\sigma_3\), since both terms \(\Delta H^A_{(T)}\) and \((\sigma_3 - \sigma_4)\) increase with \(\sigma_3\). Peak recovery stress \(\sigma_3\), however, is the function of \(\sigma_2\) (and of \(\Delta T = T_3 - T_1\)), and, furthermore, \(\sigma_2\) is the function of the effective strain \(\varepsilon = \varepsilon_2 - \varepsilon_1\).

The size of the area 1-2-3-4 in Figure 15b (which is indicative of the cycle efficiency) increases with \(\varepsilon = \varepsilon_2 - \varepsilon_1\) (i.e., increases with the distance between points 3 and 4). Conversely, if the strain \(\varepsilon\) is reduced (in the limiting case) to zero, the efficiency \(n\) becomes zero, because \(\Delta r = 0, \Delta h = 0\). Consequently by definition:
\[ \Delta H^{M \to A}_{(0)} = \Delta H_{(0)}^{M \to A} = \Delta H_{(o)}^{A \to M} \]

For this case the area 1-2-3-4 in Figure 15b reduces to a single curve between points 1 and 4, which then represents a simple strain-free thermal cycling of the (free unrestrained) Nitinol wire between the temperatures \( T_1 \) and \( T_3 \).

In the present analysis it is assumed that the latent heat of transformation \( \Delta H^{M \to A}_{(\sigma)} \) is absorbed by the Nitinol before the contraction of the wire begins (before the point 3 in Figure 15b is reached). Although this assumption is in conflict with the theorems of other investigators [8], [18], it is nevertheless supported by the experimental evidence presented by Melton and Mercier [19] and by the following observation. Figure 16 shows a dual-beam oscilloscope record of the constant-strain isothermal cycle taken from the test series (F). The electrical resistivity (higher beam) of the Nitinol wire during the engine cycle is recorded above the stress-strain diagram (lower beam). As indicated, the maximum change in resistivity occurs upon submerging the wire in the hot bath (from point 2 to point 3) and the resistivity subsequently remains nearly constant during the contraction of the wire element (point 3 to point 4). It has been well established [20] that the resistivity of Nitinol is distinctly different for the austenitic and for the martensitic phase. Moreover, the diagram in Figure 16 can be nearly duplicated when the heat input \( Q_H \) is effected by an electric pulse (see Figure 20 in the Appendix). The pulse can be timed to be completed.
before the beginning of the contraction of the wire element, and consequently positively no external heat is supplied to wire element during the shape recovery process.

On the basis of the above experimental evidence, it is proposed that during the constant-strain isothermal cycle the latent heat of phase transformation is absorbed by the constrained Nitinol wire before the beginning of the contraction, which implies that the phase transformation (Martensite $\rightarrow$ Austenite) may occur before the shape recovery event.

In the case of the constant-stress isothermal cycle, the experimental results obtained to date are inconclusive and further investigation is planned to identify the way $\Delta H_{(o)}^{M\rightarrow A}$ is absorbed during this type of cycle.

Returning now to Equations (12) and (13) we may first calculate $Q_D, Q_R$ and $Q_C$. For a trained Nitinol wire with fully developed "second memory" no stress rise results during stretching of the wire in the cold reservoir, i.e., $\sigma_2 - \sigma_1 = 0$ and $Q_D = 0$. Taking the value of the coefficient of thermal expansion from Reference [15]:

$$\alpha_T = 33 \times 10^{-6}/^\circ\text{C}$$

and the other material properties from Reference [21]:

$$\gamma = 6.45 \times 10^3 [\text{kg/m}^3], \Delta H = 5.78 \text{ cal/g}$$
and setting \((\sigma_3 - \sigma_4) = 30\text{Kpsi}\), and \(T_3 = 343^{\circ}\text{K}\) in Equation (6) gives:

\[
Q_R = 86.54 \times 10^{-3} \text{cal/g} = 0.363 \text{ Joule/g}
\]

Furthermore, assuming \(\Delta H_{A \rightarrow M} = \Delta H\) in Equation (7) yields for \(Q_C\) as the first approximation:

\[
Q_C = 0.11 \times 70 + 5.78 = 13.48 \text{ cal/g} = 55.4 \text{ Joule/g}
\]

In comparison to \(Q_C\) the value of \(Q_R\) is relatively small and significantly contributes to the efficiency of the constant-strain isothermal cycle only if \(Q_R\) is comparable to the difference between \(Q_H\) and \(Q_C\) (see Equation 12).

For the calculation of \(Q_H\) the value of \(\Delta H_{M \rightarrow A}^{(a)}\) has to be determined. Tong and Wayman [21] concluded that there will be only a small correction factor when calculating the difference between \(\Delta H_{M \rightarrow A}^{(a)}\) and \(\Delta H_{A \rightarrow M}^{(a)}\). Several investigators derived expressions for \(\Delta H_{M \rightarrow A}^{(a)}\) based on the Clausius-Clapeyron relation [22 - 25]. Furthermore, Salzbrenner and Cohen [26] pointed out the difference between the chemical and elastic component of \(\Delta H_{A \rightarrow M}^{(a)}\). Thus far, however, no calculated or measured values of \(\Delta H_{M \rightarrow A}^{(a)}\) as the function of recovery stress have been published for Nitinol. Therefore, in this study an attempt was made to determine experimentally the effect of stress on the latent heat of phase transformation.
In the test series (E) and (F) the total heat input \( Q_H \) was determined in the following way: the constant-strain isothermal cycle was repeated (at least one hundred times for every data point) at \( \varepsilon = 0.5 \) percent, 1.1 percent and 1.6 percent elongation with \( T_1 = +1^\circ C \) and \( T_3 = 51^\circ C \) held constant (test series (E)); the cycles for each \( \varepsilon \) setting were duplicated when the heat \( Q_H \) was supplied by an electric pulse instead of the hot bath (see Appendix); the voltage level of the pulse was adjusted so that the same peak recovery stress \( \sigma_3 \) was obtained as when the wire was heated in the hot bath; the product of voltage, current, and time interval of the pulse expressed in Joules/g is plotted in Figure 17a; also plotted are the data from the second test series (F) run at the same parameter settings, except for the hot bath temperature which was maintained at 71°C. When the sensible heat \( (C_p \Delta T) \) was subtracted, the data points from both test series fell on one curve as shown in Figure 17b. For comparison, the value \( \Delta H = 5.78 \text{ cal/g} = 24.2 \text{ Joule/g} \), from Reference [2], is indicated by a cross (near the vertical scale). On the basis of these tests the latent heat of transformation \( \Delta H^{M\rightarrow A}_{(\sigma)} \) appears to be strongly influenced by the magnitude of the peak recovery stress.

The curve (E) and (F) is replotted again on a larger scale in Figure 18 and extrapolated to \( \sigma_3 = 0 \) which should theoretically yield:

\[
\Delta H^{A\rightarrow M}(0) = \Delta H^{M\rightarrow A}_{(\sigma=0)}
\]
If this value could be taken as the true $\Delta H_{(0)}^{\text{A$\rightarrow$M}}$, then the energy conversion efficiency as calculated by Equation (13) should indeed be high, approaching the Carnot efficiency in isothermal cycles with peak recovery stress of about 32 Kpsi. The real value of $\Delta H_{(0)}^{\text{A$\rightarrow$M}}$ is, however, quite different if it is defined in accordance with the law of the conservation of energy: No energy can be lost during the entire cycle, and therefore the latent heat of transformation $\Delta H_{(0)}^{\text{A$\rightarrow$M}}$ (Austenite $\rightarrow$ Martensite) during the cooling period must include all the "unused" heat energy which, by definition, is the difference between the energy absorbed by the Nitinol (as the latent heat of transformation: Martensite $\rightarrow$ Austenite) during the heating period and the amount of heat that was converted to the useful mechanical work (neglecting $\Delta r$).

Based on the above definition, the latent heat $\Delta H_{(0)}^{\text{A$\rightarrow$M}}$ can be calculated from Equations (8) and (10), substituting for $\Delta h$ the mechanical work $W$, which has been determined by the planimetry of the stress-strain diagram (for each data point). The plotted results are shown as the curve $\Delta H_{(0)}^{\text{A$\rightarrow$M}}$ in Figure 18. (Note that $\Delta H_{(0)}^{\text{A$\rightarrow$M}}$ as derived by the calculation does not appear as a constant value, but as a function of $\sigma_3$). Similar curves of the latent heat of transformation ($\Delta H_{(\sigma)}^{\text{M$\rightarrow$A}}$ and $\Delta H_{(0)}^{\text{A$\rightarrow$M}}$) can be experimentally derived for other types of engine cycles, such as the constant-stress isothermal and the semi-adiabatic cycle.

At present, an attempt is being made to define the fundamental causes of energy degradation during the SME energy conversion process
and to determine whether a correlation exists between these causes and
the characteristic trend of the latent heat of transformation ($\Delta H^{M\rightarrow A}_{\gamma}$
and $\Delta H^{A\rightarrow M}_{\gamma}$) as the function of the peak recovery stress. Among the
causes of the energy degradation the following are being considered:

1) Internal friction in the lattice which causes dissipation of
the elastic strain energy. This occurs particularly when
stress and strain changes are not in phase [26].

2) The irreversibility of spontaneous thermodynamic processes,
such as spontaneous martensitic transformation. (The revers-
ible processes are never spontaneous and require careful
guidance from outside their boundaries [27].)

3) The residual internal stress fields in the lattice which
contribute to hysteresis and the loss of the pseudo-
elasticity [28].

6. PRELIMINARY INVESTIGATIONS OF VARIOUS APPROACHES TO EFFICIENCY
IMPROVEMENT

Besides the studies discussed above, a few preliminary
investigations aimed at the improvement of the energy conversion
efficiency in Nitinol have been conducted. These deal with:

a) Favorable orientation of martensite variants. b) Adiabatic
generate cycles. c) Engine cycles with heat recuperation.
a) **Favorable orientation of martensite variants**

During the martensitic phase transformation in a stress-free Nitinol wire, theoretically 24 random oriented martensite variants develop in the parent (austenitic) lattice structure. Upon subsequent heating of the wire above the transition temperature the martensite variants transform to the parent phase (austenite). However, when the martensitic (forward) transformation takes place under the action of stress (e.g., resulting from external force acting on the wire element in the direction of the wire centerline), only some preferentially oriented variants of martensite are likely to form, while the formation of others will be suppressed [29]. If it can be assumed that upon heating (reversed transformation) these preferentially oriented variants are those which most effectively contribute to the magnitude of the resulting recovery stress, then a way should be sought to assure such preferential orientation of the martensite variants also under the conditions of the actual engine cycle operation.

Unfortunately, in the practical case of relatively rapid cooling of Nitinol during the engine cycle (after contraction and relaxation of the wire element has been completed) the orientation of the variants may rather follow the direction of the resulting internal (thermal) stresses which are generally oriented perpendicularly to the centerline of the wire element. Thus far, it has not been ascertained whether or not all these variants reorient themselves in the more favorable direction during the subsequent straining of the Nitinol
wire. Perhaps it can be argued that a complete reorientation of all martensitic variants would generate additional lattice dislocations, resulting in increased hysteresis and decreased life of the wire element [28], [30] and also decreased engine cycle efficiency. On the other hand, if a method could be devised to orient the martensitic variants in the more favorable direction during the rapid cooling of the Nitinol wire, perhaps a larger recovery force could be produced upon heating of the wire element, resulting in a larger amount of mechanical work during the engine cycle.

Preliminary test results of isothermal constant-strain cycles with very slow cooling rate of the wire element indicate an improvement of the cycle efficiency by a factor of 2.0. This is interpreted as the consequence of more favorable orientation of the martensite variants due to the absence of thermal stresses during very slow cooling of the wire element in air (as compared to the fast cooling by submerging the wire in a liquid bath).

The most favorable orientation of the martensite could be expected if the isothermal engine cycle is performed entirely in the austenitic region (at a cold reservoir temperature above 50°C). This was suggested in Reference [31]. In such a case, only the stress-induced martensite would be generated during the straining of the wire, with the favorable orientation of the variants. However, the disadvantage of such a cycle is the inherently high recovery stress level and consequently short life of the Nitinol wire element.
b) **Adiabatic engine cycles**

For the realization of the highest possible thermodynamic efficiency, the Nitinol engine cycle should ideally closely approximate the Carnot cycle. The Carnot cycle consists of two adiabatic and two isothermal changes of the thermodynamic state. The heat from the hot reservoir must be supplied during the engine cycle only at the highest cycle temperature $T_3$ (isothermally), and the rejected heat must be transferred to the cold reservoir only at the lowest cycle temperature $T_1$ (isothermally). In contrast to the previously discussed isothermal engine cycle (see Figure 15), no heat is exchanged with the surroundings at any temperature intermediate between $T_3$ and $T_1$ [32]. The necessary heating of the Nitinol wire from $T_1$ to $T_3$ must be accomplished by the adiabatic heating resulting from rapid straining of the wire element. Similarly, the adiabatic cooling of the wire element should be attained by rapid contraction of the wire. Unfortunately, this type of cycle does not appear to be realizable with SME polycrystalline materials, because the phase transformation process can be accomplished (i.e., the latent heat of transformation can be absorbed) only over a definite span of the temperature range (e.g., 50°C). This means that in the strict sense of the definition the condition of a total heat input at the highest cycle temperature cannot be satisfied.

A part-way approach to the Carnot cycle can be attained by a semi-adiabatic cycle. Such a cycle is schematically shown in Figure 19a in the stress-strain coordinates and in Figure 19b in the
T-S coordinates. The cycle starts with the removal of the Nitinol wire from the cold bath and adiabatic rapid straining of the wire in air (point 1 to point 2), while the stress rises from $\sigma_1$ to $\sigma_2$, and the temperature from $T_1$ to $T_2$. Thereafter, the wire is instantly submerged in the hot bath (hot reservoir) which is maintained at the temperature $T_3$. Here the wire absorbs the latent heat of transformation and the sensible heat $C_p(T_3 - T_2)$, while the stress rises to $\sigma_3$. At this point the wire is removed from the hot bath and allowed to rapidly contract (point 3 to point 4), while the stress drops to $\sigma_4$ and the temperature to $T_4$. At the end of this interval, the original length of the wire is recovered and the power-stroke completed. Finally the wire is transferred back into the cold bath (point 1) where it is cooled to temperature $T_1$ while rejecting the latent heat of transformation and the sensible heat $C_p(T_1 - T_4)$.

Experience shows that the temperature $T_1$ must be adjusted so that only a partial martensitic transformation takes place in the cold bath. If a complete transformation is allowed, the Nitinol wire becomes too ductile and no temperature rise will be attained during the subsequent rapid straining (point 1 to point 2).

The major difficulty in realization of the semi-adiabatic cycles, aside from the necessity of accurate timing of all cycle events, is the requirement for rapid straining of the Nitinol wire. If the straining time is more than one-half of a second, much of the heat (which was generated by straining the wire) is lost by convection to
the surrounding air and the adiabatic temperature rise (point 1 to point 2) is reduced. Rapid straining, however, may cause nonuniform stress and temperature distribution in the wire, and this in turn may cause an increase of internal friction in the lattice, leading to a decrease of the efficiency and life of the wire element.

The adiabatic temperature rise that can be accomplished by rapid straining of the presently available Nitinol wire is quite limited. This is because the strain-temperature coefficient of adiabatic heating (resulting in the heat of elastic deformation) is small. As the first approximation \( \Delta T_D \) can be calculated from Equation (4) dividing the heat of elastic deformation \( Q_D \) by the specific heat of Nitinol:

\[
\Delta T_D = \frac{(\sigma_2 - \sigma_1) \alpha_T T_1}{C_p \gamma J}
\]  

(16)

Simultaneously, an additional temperature rise \( \Delta T_M \) is effected by the exothermic latent heat of transformation, originating from the stress-induced martensite which grows during the stressing of the wire element. \( \Delta T_M \) can be calculated only if the amount of the stress-induced martensite \( (\%)_M \) is known:

\[
\Delta T_M = \frac{(\%)_M \Delta H_{A \rightarrow M}}{C_p}
\]  

(17)

(where \( C_p \) is taken as the average value). The total temperature rise is then:
\[ (T_2 - T_1) = \Delta T_D + \Delta T_M \] (18)

Preliminary tests were conducted to determine the total temperature rise \((T_2 - T_1)\) experimentally. For 1.0 percent strain effected in 65 ms (starting at \(T_1 = 24^\circ C\)) the total temperature rise was about 4°C. The method employed in these tests will be published later. The present result is considered tentative, and additional tests employing other measurement methods are in preparation.

The efficiency of the semi-adiabatic cycle can be written as:

\[ n = 1 - \frac{Q_C}{Q_H} = 1 - \frac{C_p(T_4 - T_1) + AH_{M \Rightarrow H}^{A \Rightarrow M \Rightarrow M}}{C_p(T_2 - T_2) + AH_{H \Rightarrow 0}^{H \Rightarrow M \Rightarrow M \Rightarrow M \Rightarrow A}} \] (19)

Comparing Equation (19) to (13), and assuming all other factors the same, it can be seen that an efficiency improvement over the isothermal cycle can be expected only if the reduction of the sensible heat \(C_p(T_3 - T_2)\) and \(C_p(T_4 - T_1)\) relative to \(C_p(T_3 - T_1)\) is substantial. This, of course, depends on the magnitude of the adiabatic temperature rise \((T_2 - T_1)\) and the temperature drop \((T_4 - T_3)\), respectively.

Preliminary tests of the semi-adiabatic cycle have been conducted; however, no data indicating a substantial efficiency improvement were obtained to date.

c) Engine cycles with heat recuperation

One evident approach to efficiency improvement is based on the principle of heat recuperation during the engine cycle. The objective is to transfer the heat available from a Nitinol wire element which
has just completed the engine cycle (end of power stroke) to another wire element which has been strained and is ready to be heated and to start the power stroke. However, because of the relatively low heat conductivity of Nitinol and the small temperature gradient between the wires in a (counterflow) heat exchanging relationship, the heat transfer rate is low and presents a limit to the potential efficiency improvement. Depending on the sophistication and the type of the engine design concept, an efficiency improvement by a factor of 1.5 to 2.5 appears feasible.

7. DISCUSSION AND CONCLUSION

In the studies reported here, the efficiency of the conversion of heat to useful mechanical work in a "solid state" Nitinol heat engine has been experimentally investigated. Various thermodynamic engine cycles were performed on a specially designed cycle-simulator apparatus. In each test series, a specific range of test parameters was covered, and each specific setting of the test parameters was repeated over several hundreds of cycles.

The highest thermodynamic efficiency on the order of 1.2 percent (approximately 6 percent of Carnot efficiency) has been demonstrated, with Nitinol wire life expectancy of about $10^4$ cycles. At more conservative stress and strain levels, lower thermodynamic efficiency resulted (about 0.5 percent); however, the wire life expectancy could be estimated to exceed $10^6$ cycles.
These experimentally determined efficiencies are not in agreement with the theoretical calculations published in the References [8-11]. The reason for this discrepancy might be as follows: The referenced calculations are based on the premise that the chemical free energy difference between the martensitic and the austenitic phase represents the maximum energy which is theoretically available for conversion to useful mechanical work. Although the chemical free energy difference constitutes the "driving force" for the phase transformation, it does not present a sufficient basis for the analytical determination of the energy conversion efficiency.

For the determination of the efficiency of any thermodynamic cyclic process, it is necessary to adequately define the sequence of the events and the mode of the energy transaction during each event of the specific type of thermodynamic cycle under consideration. The analysis of the constant-strain isothermal cycle presented in this study is an example of such a procedure. For the definition of the mode of energy transaction during the individual events of the isothermal cycle, several models have been considered and subjected to experimental verification. As a result, the following postulates were formulated and proposed:

1) The effective useful work obtainable during the (constant-strain) isothermal cycle is equal to the difference between the latent heat of reverse transformation $\Delta H_{M\rightarrow A}^{\text{(o)}}$ (during increasing stress) and the latent heat of forward transformation $\Delta H_{A\rightarrow M}^{\text{(o)}}$ (during "stress-free" state).
An additional small contribution comes from the difference between the heat of elastic deformation $Q_D$ (during the straining of the SME element) and the heat of elastic recovery $Q_R$ (during the contraction of the SME element).

2) During the constant-strain isothermal cycle (the most simple Nitinol engine cycle), the latent heat of reverse transformation $\Delta H_{M\rightarrow A}^{(\sigma)}$ (Martensite $\rightarrow$ Austenite) is absorbed by the SME material before the shape recovery (contraction of the wire element) takes place.

3) The magnitude of the latent heat of reverse transformation $\Delta H_{M\rightarrow A}^{(\sigma)}$ (Martensite $\rightarrow$ Austenite) is a strong function of the peak recovery stress.

4) The magnitude of the (apparent) latent heat of forward transformation $\Delta H_{A\rightarrow M}^{(\sigma)}$ (Austenite $\rightarrow$ Martensite) under the zero external force condition (after the contraction of the wire element) is not constant, as would be expected for an ideal SME material. Because of the nonideal behavior of the SME material (Nitinol), the magnitude of the (apparent) latent heat of forward transformation increases with the increasing peak recovery stress. This increase is presently interpreted as the consequence of the energy degradation in the Nitinol lattice during the engine cycle.

In accordance with the above postulates, Equations (13) and (14) yield efficiency values which are consistent with the experimental results reported here. It is evident that extensive basic and
materials research is needed for a better understanding of the energy conversion process in Nitinol. An important advancement in this direction is presented in Reference [26], which elucidates the effect of the grain boundaries in a polycrystalline (versus single crystal) Cu-Al-Ni alloy on the internal frictional resistance, on the stored elastic strain energy in the lattice, and on the temperature range of the martensitic phase transformation. Phase transformation studies of a single crystal Nitinol alloy have been suggested and are in preparation [33].

In summary, the following conclusions can be drawn:

a) Generally, only the heat engines operating on adiabatic thermodynamic cycles can theoretically approach the Carnot cycle efficiency.

b) Because of the very limited temperature rise during the wire straining and the relatively large temperature range of the Nitinol phase transformation, the Nitinol heat engine is incapable of operating on an adiabatic cycle and therefore is restricted (for all practical purposes) to the isothermal cycle.

c) The isothermal cycle is inherently (thermodynamically) inefficient, no matter whether fluids or solid-state materials are employed as the working medium.

d) The magnitude of the latent heat of reverse transformation of Nitinol \( \Delta H_M^{\text{MA}} \) substantially increases with increasing peak recovery stress. As the consequence of this increase of heat which is absorbed during the engine cycle, the efficiency is further lowered.
e) The potential engine efficiency $\eta$ is ultimately limited by the requirement of an acceptable life of the Nitinol wire element. The capacity of Nitinol to perform mechanical work cannot be utilized beyond the limits of the peak stress and strain set by this requirement.

f) Any improvement of the Nitinol material in respect to the strength and durability would extend the permissible peak stress and strain limits and therefore result in an improvement of the thermodynamic engine efficiency $\eta$ (as shown in Figure 8).

g) In planning future research, perhaps the most promising direction would be towards the development of new Nitinol alloys with a very narrow temperature range of the phase transformation. Such alloys would permit engine operation at a small temperature difference between the hot and cold reservoir, with the result of a higher $\eta/\eta_c$ ratio. This would greatly enhance the potential usefulness of the Nitinol heat engine in application to heat sources with a very small temperature gradient.
8. NOMENCLATURE

$C_p$  specific heat of Nitinol [0.11 cal/g°C]

$E$  elongation of Nitinol wire after straining [mm]

$F$  force exerted by Nitinol wire at peak stress $\sigma_3$ [kg]

$H$  enthalpy

$\Delta H$  latent heat of phase transformation of undeformed (unstretched) and unrestrained Nitinol wire [5.78 cal/g]

$\Delta H_{A\rightarrow M}^{(o)}$  latent heat of forward phase transformation (austenite $\rightarrow$ martensite) at zero external force, after the contraction (shape recovery) of the Nitinol wire.

$\Delta H_{M\rightarrow A}^{(\sigma)}$  latent heat of reversed phase transformation (martensite $\rightarrow$ austenite) of a prestrained Nitinol wire during the rise of a recovery stress $\sigma_3$

$J$  mechanical equivalent of heat [427.8 mk/g/kcal]

$L$  length of the Nitinol wire [mm]

$L_{g}$  length of Nitinol wire per 1 gram weight

$\Delta L$  linear change of the wire length during the contraction ($\Delta L = E$)

$Q_c$  total heat input to the Nitinol wire during one engine cycle

$Q_c$  heat rejected by the wire in the cold bath (cold reservoir)

$Q_d$  exothermic heat of elastic deformation (stretching) of the Nitinol wire at constant temperature

$Q_{[g]}$  total heat input per 1 gram of Nitinol

$Q_h$  heat absorbed by the Nitinol wire in the hot bath (hot reservoir)
endothermic heat of shape recovery, absorbed by the Nitinol wire during the elastic contraction at constant temperature

S entropy

T₁ temperature of the cold bath

T₃ temperature of the hot bath

ΔT = T₃ - T₁

ΔT_D adiabatic temperature rise due to the heat of elastic deformation in rapidly strained Nitinol wire

ΔT_M adiabatic temperature rise due to the latent heat of phase transformation (austenite ↨ martensite) in rapidly strained Nitinol wire

U internal energy

W useful mechanical work produced by Nitinol wire during the engine cycle [mkg]

α work diagram factor (ratio of actual diagram area to the ideal diagram area)

αₜ coefficient of linear thermal expansion of Nitinol in the transition region [°C⁻¹]

γ density of Nitinol [0.234 lb/in³]

ε = ε₂ - ε₁, effective strain of the Nitinol wire in percent

ε₁ initial strain

ε₂ final strain

η thermodynamic engine cycle efficiency

η_c Carnot cycle efficiency

σ₁ initial stress [kpsi]
$\sigma_2$ stress at the end of the straining period

$\sigma_3$ maximum peak recovery stress

$\sigma_4$ residual stress after the contraction (shape recovery) of the Nitinol wire
9. REFERENCES


33. C. M. Gilmore, Private Communication. (This research was suggested and is in preparation by Professor Gilmore, George Washington University, School of Engineering and Applied Sciences, Washington, D.C.).
APPENDIX

Determination of the heat input $Q_h$ to the Nitinol wire during the engine cycle

The heat is supplied to the Nitinol wire element during the engine cycle at the instant when the wire is submerged in the liquid of the hot reservoir. It would be very difficult to attempt to measure directly (with any accuracy) the amount of heat which the wire absorbs. Therefore, the following method of wire heating and heat input measurement has been employed in this study. The method consists of two steps:

1) First, the wire is subjected to the constant-strain isothermal cycles (in accordance with the chosen test parameters) on the Cycle Simulator, while it is heated in the standard way by submerging it in the hot bath. The stress-strain diagram (lower trace) and the wire ohmic resistance (upper trace) are recorded on the screen of a dual-beam oscilloscope. See Figure 20.

2) Then (while the cycling is continued) the hot bath is removed and the wire is heated (while in air) by an electric pulse at the proper instant during each of the following cycles. All other test parameters are kept unchanged. The DC current of the electric pulse is timed and the voltage is adjusted so that the same peak recovery stress is obtained as when the wire has been heated in the hot bath. At this time the stress-strain diagram is again recorded. The product of the current, voltage
and time interval of the electric pulse yields the total heat input $Q_H$ in Watt-sec (= Joule) to the wire element. The electric pulse record is shown in Figure 21.

The final record (see Figure 20) consists of the traces of a number of repeated cycles with heating of the wire by an electric pulse, which are superimposed over the traces of a number of repeated cycles when the wire has been heated in the hot bath. (Record in Figure 20 was obtained on Tektronix 7623A storage oscilloscope).

Part of the stress-strain diagram—namely, the lines which slope downward from right to left—represents the contraction of the wire element after heating. The slightly convex line resulted when the wire was heated in the hot bath, and the slightly concave line (lower line) resulted when the wire was heated by the electric pulse. This difference is partially due to the fact that when the Nitinol wire element is heated in the hot bath, it is also allowed to contract in the hot bath, and consequently it absorbs an additional small amount of heat during the wire contraction. This additional heat, which is the heat of the elastic shape recovery $Q_R$ (see text), contributes a modest amount of energy to the engine cycle, which is also partially converted to useful mechanical work. As a result, the area of the stress-strain diagram under the convex line is slightly larger (about 10 percent).

Figure 20 also presents the following information: cold reservoir temperature $T_1 = +2^\circ C$, hot reservoir temperature $T_3 = +52^\circ C$, cyclic elongation $\Delta L = 6$ mm of the wire element corresponding to
1.6 percent strain. The difference in the ohmic resistance of the Nitinol wire (upper trace) between the martensitic (lower line) and the austenitic (upper line) phase is 0.27 ohms. (The distance between the short horizontal calibration mark and the lower line indicates 0.1 ohms.) This corresponds to about 15 percent change in the absolute resistance of the Nitinol wire element.

The upper trace in Figure 21 represents the current pulse, the middle trace and the voltage pulse, and the lowest trace the time interval of the wire contraction. The duration of the heating pulse and of the wire contraction is about 350 ms each. Between the end of the heating pulse and the start of the wire contraction is a small time overlap—about 40 ms—which was determined experimentally for the optimal utilization of the pulse energy. The current was read across a calibrated shunt and the voltage across the terminals of the Nitinol wire element. The signal for the wire contraction was monitored directly from the electronic pulse control system of the Cycle Simulator.

The heat losses from the Nitinol wire element during the heating pulse and during the wire contraction period were determined as follows: During one test cycle the wire element was not allowed to contract, but was held constrained after the completion of the electric heating pulse. The peak recovery stress $\sigma_3$ was displayed on the oscilloscope screen with the horizontal sweep of the beam adjusted to 200 ms per cm. The rise of the recovery stress during the heating pulse and the subsequent decay of stress due to the heat
losses to the surrounding air as the function of time are shown in Figure 22.

The heat losses were calculated from the slope of the asymptotic stress decay curve. For the total period of the electric pulse and the subsequent wire contraction period (700 ms), the heat losses amounted to approximately 5 percent of the pulse energy.
Fig. 1. Cycle Simulator experimental system.
Fig. 2. Design drawing of the Cycle Simulator.
Legend: 1 Nitinol wire, 2 sliding arm,
3 fixed arm, 4 strain gage, 5 lead screw,
6 driving nut, 7 hot reservoir, 8 cold
reservoir, 9 shaft, 10 linear ball bearings,
11 lead screw servomotor, 12 shaft servomotor,
13 tachometer-generator, 14 shaft sprocket
wheel, 15 lead screw drive, 16 front support
bearing, 17 rear support bearing, 18 positioning
microswitches, 19 positioning cam.
Fig. 3. Laboratory experimental set-up, including Cycle Simulator, electronics and video data recording system.
Fig. 4. Video record of a typical constant-strain isothermal cycle.
Fig. 5. Constant-strain isothermal cycle resulting when heat is supplied by electric pulse.
Fig. 6. Stress-limited isothermal cycle. Heat supplied by electric pulse.
Fig. 7. Constant-stress isothermal cycle.
Fig. 8. Thermodynamic efficiency of the energy conversion in Nitinol as the function of peak stress $\sigma$ ($\sigma = \sigma_3$), and percent elongation $\varepsilon$ of the wire element.
Fig. 9. Recovery peak stress during various engine cycles as the function of the hot reservoir temperature.
Fig. 10. Useful mechanical work produced by various cycles as the function of peak recovery stress.
Fig. 11. Thermodynamic engine cycle efficiency as the function of the hot reservoir temperature.
Fig. 12. Ratio of the thermodynamic engine cycle efficiency to the Carnot cycle efficiency as the function of the hot reservoir temperature.
Fig. 13. Thermodynamic engine cycle efficiency as the function of heat input.
Fig. 14. Thermodynamic engine cycle efficiency as the function of peak recovery stress.
Fig. 15. Schematic diagram of the constant-strain isothermal cycle.
Fig. 16. Dual-beam oscilloscope record of the Nitinol resistivity (upper trace) during the constant-strain isothermal cycle (lower trace).
Fig. 17. Total heat input and the latent heat of phase transformation as the function of the peak recovery stress during the constant-strain isothermal cycle.
Fig. 18. Latent heat of reverse transformation (martensite → austenite) and the "apparent" latent heat of forward transformation (austenite → martensite) as the function of the peak recovery stress.
Fig. 19. Schematic diagram of the semi-adiabatic cycle.
Fig. 20. Determination of the heat input to the Nitinol wire during the constant-strain isothermal cycle.
Fig. 21. Current and voltage pulses for heating of the Nitinol wire element, and the wire contraction timing trace.
Fig. 22. Recovery peak stress rise during the electric heating pulse and the subsequent stress decay due to the heat losses from the Nitinol wire element.
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