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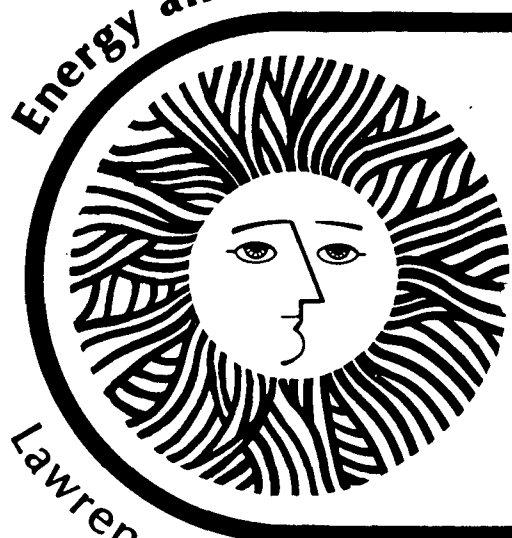
Thermal Conversion Efficiency of
An Ideal Thermoelastic Marmem*
Cycle

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# THERMAL CONVERSION EFFICIENCY OF
# AN IDEAL THERMOELASTIC MARMEM* CYCLE

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## ABSTRACT

The thermal conversion efficiency of an ideal stress-strain-temperature cycle based on the mechanical shape memory effect associated with a thermoelastic martensite transformation (thermoelastic marmem cycle) has been studied.  A relationship between the upper limit of the thermal efficiency and a set of materials properties has been derived. It is shown that a higher thermoelastic marmem efficiency and a closer approach to the corresponding Carnot efficiency are favored by:

1) higher yield stress of the high temperature phase,

2) larger recoverable strain,

3) smaller transformation temperature range and thermal hysteresis associated with the transformation, and

4) smaller transformation latent heat.

The thermal efficiency has been calculated for a cycle utilizing a Ti-50.4 at. pct. Ni alloy.  The highest efficiency for this particular alloy was found to be about 9%; this amounts to 45% of the corresponding Carnot efficiency.  Thus it is concluded that efficiencies can be obtained which are comparable with those of cycles operating at small temperature differences with fluids as working media.

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* Marmem is derived from Martensite Memory (C. M. Wayman and K. Shimizu, Met. Sci. J. 6 (1972) 175).

1. Introduction

The mechanical shape memory effect exhibited by a large number of alloys is a phenomenon associated with thermoelastic martensite transformations [1]. A demonstration of the memory effect involves:

(a) inducing a permanent strain within a certain range at a lower temperature where the martensite phase is thermodynamically stable, followed by

(b) heating across the martensite → high temperature phase transformation temperature range.

During heating and as the martensite reverts to the high temperature phase, the strain is recovered. Complete strain recovery is achieved when the reversion of martensite is completed. Thus, the martensite transformation has an important effect on the stress-strain-temperature behavior of the material. This is shown schematically in Fig. 1. The stress $\sigma_1$ required to induce a strain $\varepsilon$ within the recoverable range at a lower temperature where the martensite phase is thermodynamically stable in the absence of stress, is much smaller than the corresponding stress $\sigma_2$ at a higher temperature where the martensite phase is stable only in the presence of stress. The stress build-up during heating ($\sigma_2 - \sigma_1$ in Fig. 1) is referred to as the recovery stress and is defined as the stress required to counterbalance the driving force of the martensite → high temperature phase transformation. This stress-strain-temperature behavior can thus be considered to be due to:

(1) Reversibility of the deformation modes that accomodate the strain within the recoverable range [2-4], and

(2) Increasing the thermodynamic instability of the martensite phase as the temperature increases within the range

$A_s$ - $A_f$*.

Therefore, in principal, a shape memory alloy can be made to perform the function of converting heat into useful mechanical work by subjecting it to an appropriate stress-strain-temperature cycle in a solid state heat engine. Recently, versions of solid state heat engines comprising shape memory alloys as working media have been demonstrated [5-7]. Due to the relatively small transformation temperature range (tens of degrees), such heat engines may prove to be important in converting low temperature, large heat sources such as solar energy. The competitive applicability of a shape memory alloy in a solid state heat engine can be measured by:

(1) thermal efficiency,

(2) work output per mass unit, this partially determines the

 power output, and

(3) fatigue life.

Recently, attempts have been made to calculate the thermal efficiency of a particular stress-strain-temperature cycle [8-10]. In these calculations, the work output was regarded as being the work done by an arbitrary constant force during heating, and the results were inconclusive. In the present investigation, the thermal efficiency of an ideal cycle has been examined with reference to the recovery stresses generated by the material during heating.

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*$A_s$ and $A_f$ are the temperatures at which the reversion of martensite to the high temperature phase starts and finishes, respectively, during heating. $M_s$ and $M_f$ are the temperatures at which the transformation to martensite starts and finishes, respectively, during cooling. In the absence of an external stress, these temperatures will be given the superscript o, and in the presence of an external stress they will be given the superscript $\sigma$.

## 2. Ideal Thermoelastic Marmem Cycle

The path of an ideal thermoelastic marmem cycle that gives the maximum work output for a given recoverable strain is shown schematically on the stress-strain plot of Fig. 2a. The microstructural changes which occur during the entire cycle are illustrated in Fig. 2b. The path of the cycle consists of two isotherms, 234 and 51, and two isochores, 45 and 12 (an isochoric process is one during which no external work is exchanged between the system and its surroundings). The working medium is a polycrystalline shape memory alloy.

### 2.1 Temperature difference across the cycle

The cycle is assumed to operate between the temperatures $A_f^\sigma$ and $M_f^O$. It is assumed that upon cooling to the $M_f^O$ temperature, all the crystallographically equivalent martensite variants form with equal probability. Therefore, in the absence of an external stress, the material does not acquire a net macroscopic strain relative to the point where it consists entirely of the high temperature phase at the $A_f^\sigma$ temperature.

Thus, the lower temperature of the cycle is fixed by the $M_f^O$ temperature. It has been shown theoretically [11] and experimentally [1] that the transformation temperatures increase linearly with increasing stress; therefore,

$$A_f^\sigma = A_f^O + C\sigma \ldots \tag{1}$$

where C is a constant and $\sigma$ is an external stress. In the discussions which follow, we assume that a heat sink exists at the $M_f^O$ temperature and a heat source(s) exists at the appropriate $A_f^\sigma$ temperature.

## 2.2 Procedure of the cycle

Referring to Fig. 2, the cycle consists of the following steps:

$1 \rightarrow 2$  The material is cooled from the $A_f^\sigma$ to the $M_f^O$ temperature to transform it almost entirely to martensite in the absence of an external stress.

$2 \rightarrow 4$  A strain $\varepsilon$ (excluding the normal elastic strain) within the recoverable range is induced by applying an external stress $\sigma_1$ and then the stress is released at the $M_f^O$ temperature.

$4 \rightarrow 5$  The material is heated to the $A_f^\sigma$ temperature while entirely constraining the strain $\varepsilon$.  This requires a continuously increasing external stress, $\sigma_r$, to counterbalance the driving force of the martensite $\rightarrow$ high temperature phase transformation (the driving force arises from the free energy difference between the martensite and high temperature phase).  Recently, it has been shown that $\sigma_r$ achieves its maximum value at the $A_f^\sigma$ temperature and that this maximum can be expressed as [12]:

$$\sigma_{r_{max}} = \sigma_y^{htp} \, [1 - \exp^{-N\varepsilon}] \qquad (2)$$

where $\sigma_y^{htp}$ is the yield stress of the high temperature phase and N is the number of crystallographically equivalent martensite variants that exist prior to straining.

$5 \rightarrow 1$  At the $A_f^\sigma$ temperature, the external stress, $\sigma_{r_{max}}$, is infinitesimally decreased.  Therefore, the driving force of the transformation overcomes the external stress and thus the martensite reverts to the high temperature phase

and the strain $\varepsilon$ is recovered. During this process, work W, is done on the surroundings and latent heat of the transformation, $\Delta H$, is absorbed. As the transformation to the high temperature phase and strain recovery are completed, the external stress, $\sigma_{r_{max}}$ $(\sigma_{r_{max}} < \sigma_y^{htp})$ is released and the material becomes ready to repeat the cycle.

## 3. Thermal Conversion Efficiency

Referring to Fig. 2a, the maximum useful work, W, per unit volume per cycle, can be expressed as:

$$W = \sigma_y^{htp} (1 - exp^{-N\varepsilon}) \cdot \varepsilon \tag{3}$$

Thus, a higher work output is favored by a higher yield stress of the high temperature phase and a higher recoverable strain. The total heat absorbed by the material during the entire cycle, $\Delta Q$, is given by

$$\Delta Q = \Delta H + \overline{C}p [A_f^\sigma - M_f^O]$$

where $\overline{C}p$ is the average specific heat of the material over the temperature range $A_f^\sigma - M_f^O$.

This can be rewritten as:

$$\Delta Q = \Delta H + \overline{C}p[ (A_f^O - A_s^O) + (A_s^O - M_f^O) + C_y^{htp} (1 - exp^{-N\varepsilon})], \tag{4}$$

$(A_f^O - A_s^O)$ is the transformation temperature range in the absence of an external stress and $(A_s^O - M_f^O)$ is a measure of the thermal hysteresis associated with the transformation.

The thermal efficiency $\eta_{th.}$ can thus be written as

$$\eta_{th.} = \frac{\sigma_y^{htp} (1 - \exp^{-N\epsilon}) \cdot \epsilon}{\Delta H + \overline{C}p \ [ (A_f^O - A_s^O) + (A_s^O - M_f^O) + C\sigma_y^{htp} (1 - \exp^{-N\epsilon})]} \tag{5}$$

The corresponding Carnot efficiency, $\eta_c$, is given by:

$$\eta_c = 1 - \frac{M_f^O}{A_f^\sigma} \tag{6}$$

It can be concluded from equations (5) and (6) that a higher thermoelastic marmem efficiency and a closer approach to the corresponding Carnot efficiency are expected to be favored by:

(1) higher yield stress of the high temperature phase,

(2) larger recoverable strain,

(3) smaller transformation temperature range and thermal hysteresis associated with the transformation, and

(4) smaller latent heat.

Fig. 3 shows schematically a desirable thermal hysteresis loop (a) vs. an undesirable one (b).

## 4. Application to a Ti-50.4 at. pct. Ni alloy

Some of the properties which determine the thermal efficiency as depicted from equation (5) have been measured for a Ti-50.4 at. pct. Ni alloy. The specimens in the form of wires, 0.5 mm in diameter, have been annealed at 600° C. for 24 hours in vacuum furnace (about $10^{-5}$ mm Hg) and then furnace cooled to room temperature.

The transformation temperatures and their functional dependence on stress have been measured using a specially designed laser-beam dilatometer. It has been observed that the transformation temperatures

during cooling and heating increase linearly with increasing stress at about the same rate. The transition entropy $\Delta S$ has been calculated from the rate of change of the transformation temperatures with stress and a modified Clausius-Clapeyron equation. The latent heat of the transformation at the equilibrium transition temperature $(T_O)$ has been calculated from $T_O \Delta S$. The equilibrium transition temperature, $T_O$, has been approximately determined from [13]

$$T_O = M_s^O + \frac{1}{2} [A_s^O - M_f^O] \ .$$

The yield stress of the high temperature phase and the recoverable strain range have been determined from tensile stress-strain data. The yield stress of the high temperature phase has been observed to be nearly independent of temperature within the temperature range of interest. A similar result has been reported for other Ni-Ti alloys [14]. This is consistent with the relatively high melting point of Ni-Ti alloys near the equiatomic composition (about 1300 C. [15]). The results of these measurements are summarized in Table I.

Table I

| Transformation Temperatures, C° | $M_s^O$ | $M_f^O$ | $A_s^O$ | $A_f^O$ | $T_O$ |
|---|---|---|---|---|---|
| | 24 | 5 | 26 | 33 | 35 |
| $C \equiv \dfrac{dA_f}{d\sigma}$, C°/(kg/mm²) | 1.14 | | | | |
| Transition entropy, $\Delta S$ (cal/gm. atom/deg) | 1.0 | | | | |
| latent heat, $\Delta H$ at 35°C (cal/gm. atom) | 308* | | | | |
| $\sigma_y^{htp}$ (kg/mm²) | 42.0 | | | | |
| Maximum recoverable strain, % | 8 | | | | |

* For a Ti-51 at. pct. Ni alloy a value of 307 cal/gm. atom at 40°C was reported (F. E. Wang, W. T. Buehlerland, and P. J. Pickert, J. Appl. Phys. 36 (1965) 3232). 1 gm. atom = 53.3 gms.

The number of crystallographically equivalent martensite variants, N, has been taken to be 24. This number follows from the crystallographic theory of the martensite transformation in a Au-47.5 at. pct. Cd alloy [16]. The crystallographic features of the transformation in Ni-Ti alloys have been observed to be very similar to those in a Au-47.5 at. pct. Cd alloy [17, 18].

The average specific heat has been taken to be 5 cal/gm. atom/deg. from the available experimental data [18]. In the calculation of the thermal efficiency, it has been assumed that the latent heat of the transformation is independent of temperature. This assumption is justified in view of the observed negligible change in specific heat upon the transformation [18].

Thus, the highest efficiency for the cycle of Fig. 2 and the particular alloy considered has been calculated using equation (5), and the data of Table I. This has been found to be about 9% (the work output is 4.3 J/gm) for $A_f^\sigma = 74°C$ and $M_f^o = 5°C$. The corresponding Carnot efficiency is 20%. Therefore, the thermoelastic marmem efficiency amounts to 45% of the corresponding Carnot efficiency. This result is comparable with those of cycles operating at comparable temperature differences with fluids as working media [19, 20].

It is expected that, with selecting or designing shape memory alloys that have better combinations of properties, higher efficiencies can be obtained. Furthermore, it is expected that solid state heat engines with shape memory alloys as working media are rather simple, since they do not require boilers and heat exchangers; they are also environmentally acceptable. It should be noted, however, that the

fatigue strength may limit the amount of strain that the material can sustain for millions of cycles without failure, although deformation by motion of twin boundaries [2] is expected to result in an extended fatigue life.

## 5. Conclusions

The thermal conversion efficiency of an ideal thermoelastic marmem cycle based on the mechanical shape memory effect associated with thermoelastic martensite transformations has been studied. A relationship between the efficiency and a set of materials properties has been derived. It is shown that a higher efficiency and a closer approach to the corresponding Carnot efficiency are favored by:

(1) higher yield stress of the high temperature phase,

(2) larger recoverable strain,

(3) smaller transformation temperature range and thermal hysteresis associated with the transformation, and

(4) smaller transformation latent heat.

The efficiency has been calculated for a Ti-50.4 at. pct. Ni alloy and it is concluded that efficiencies can be obtained (9%) which are comparable with those of cycles operating at small temperature differences with fluids as working media.

## Acknowledgments

Division of the Lawrence Berkeley Laboratory, University of California, Berkeley.

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## Figure Captions

Fig. 1 Typical tensile-stress-strain diagrams of a shape memory alloy at different temperatures within the temperature range $M_f^O - A_f^\sigma$.

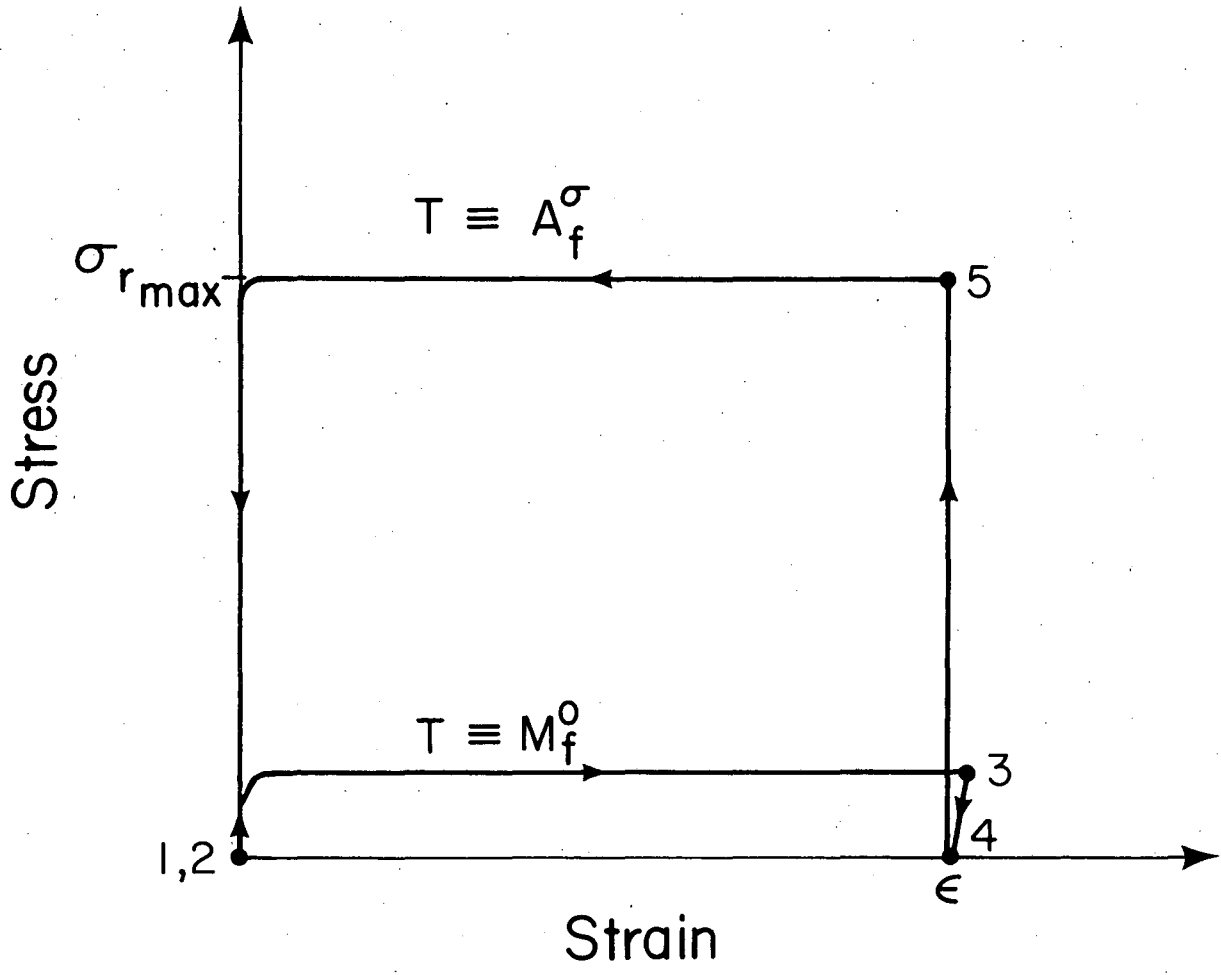Fig. 2a Ideal stress-strain-temperature cycle in two dimensions.

Fig. 2b Schematic illustration of the microstructural changes which occur during the cycle of Fig. 2a; (1) high temperature phase at $A_f^\sigma$ temperature in the absence of an external stress; (2) thermal martensite at the $M_f^O$ temperature; (3,4) deformed martensite at the $M_f^O$ temperature; (5) deformed martensite at the $A_f^\sigma$ temperature in the presence of an external stress $\sigma_{r_{max}}$.

Fig. 3 Thermal hysteresis loops associated with the martensite transformation; loop (a) favors higher thermoelastic marmem efficiency than loop (b).
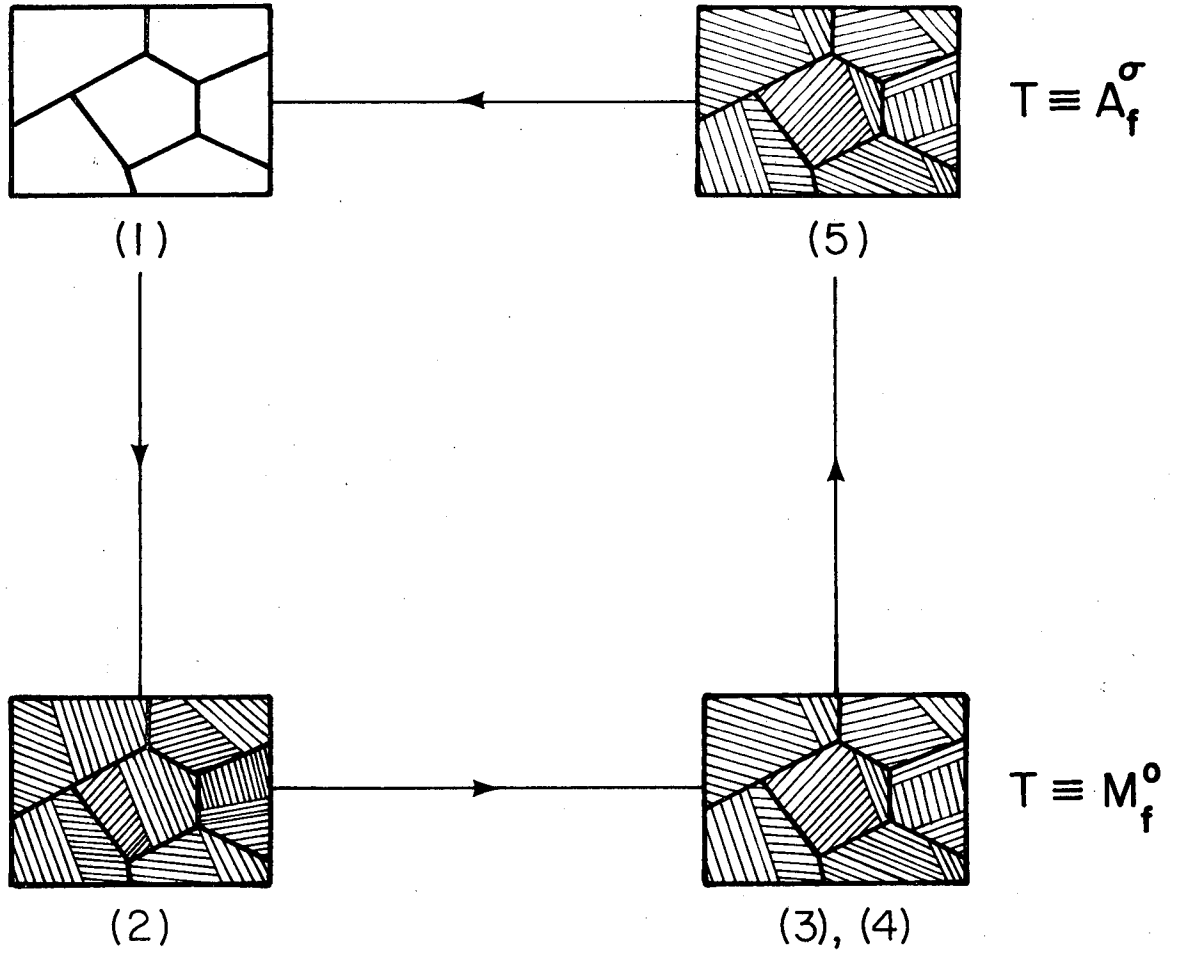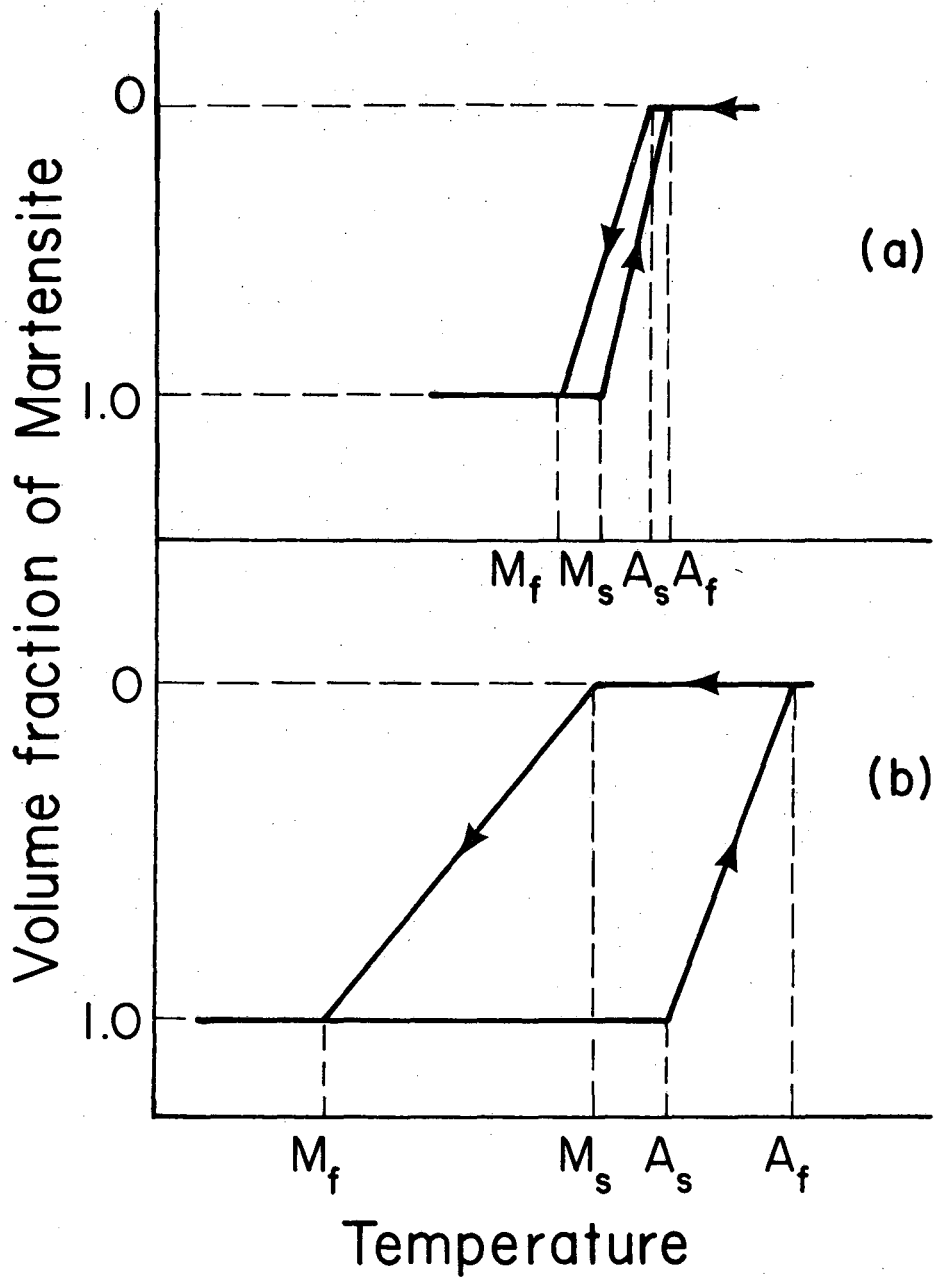
Fig. 1

Fig. 2a

XBL 787-1248

$T \equiv A_f^{\sigma}$

(1)   (5)

$T \equiv M_f^o$

(2)   (3), (4)

XBL 787-1252

Fig. 2b

Fig. 3

XBL 787-1247