

Lawrence Berkeley National Laboratory

Recent Work

Title

ON THE THERMODYNAMICS OF THE SHAPE MEMORY ALLOYS

Permalink

<https://escholarship.org/uc/item/2bb3g4c7>

Author

Weres, Oleh.

Publication Date

1975-11-01

Submitted to Acta Metallurgica

RECEIVED
LAWRENCE
BERKELEY LABORATORY

LBL-3297
Preprint c. 2

DEC 3 1975

LIBRARY AND
DOCUMENTS SECTION

ON THE THERMODYNAMICS OF THE SHAPE MEMORY ALLOYS

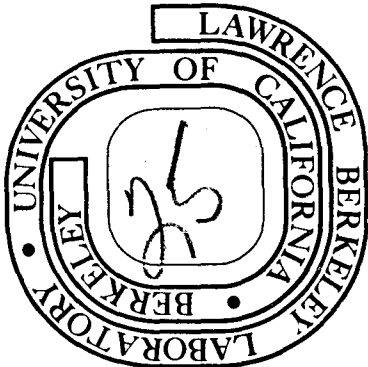
Oleh Weres

November 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, ~~Ext 5545~~*



LBL-3297

c. 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

ON THE THERMODYNAMICS OF THE
SHAPE MEMORY ALLOYS*

Running Title: SMA Thermodynamics

by

Oleh Weres

November, 1975

University of California
Lawrence Berkeley Laboratory
Energy and Environment Division
Berkeley, California 94720, USA

ABSTRACT

A theory of the fundamental thermodynamic properties of the shape memory alloys is constructed on the basis of their stress-strain properties. The pre-Martensitic phenomena are identified to be critical point phenomena which occur at zero stress and the critical temperature T_C , above which two phases may coexist under stress, and below which only one phase, Martensite, can exist.

The deviation of the pre-Martensitic phenomena in polycrystalline NiTi from the simple "ideal" form predicted by the theory is explained in detail in terms of the effects of internal stresses and "training". It is argued that $T_C = M_f$.

Several mechanisms are proposed to explain the "nonideal" behavior of those SMA's which transform to a twinned Martensite and polycrystalline specimens. It is concluded that "twinning" SMA's are intrinsically incapable of ideal behavior near T_C , which appears to be borne out by experiment.

The practical possibilities of SMA heat engines are discussed and it is concluded that, with a proper choice of cycle and good enough material, there is no fundamental limitation upon their potential thermal efficiency beyond that imposed by the Second Law of Thermodynamics.

*Work performed under the auspices of the U. S. Energy Research and Development Administration.

I. Introduction

The general approach of a theoretician attempting to explain the properties of a complex system is to draw from the available data those facts which seem most significant, develop a rigorous model of these "essential" phenomena and then to back up and explain in as far as possible the remaining facts in a manner consistent with the basic model.

The "essential" thermodynamic properties of any material are the properties of an imaginary "ideal" specimen whose properties are everywhere singly defined. In the following section we extract the stress-strain-temperature relationship of an ideal monocrystal of SMA under uniaxial stress from actual stress-strain data. In this specific application "ideality" requires that the stress at any given combination of strain and temperature be independent of the path by which that ϵ - T point was reached. In the terminology of Tong and Wayman¹, the "non-chemical free energy" ΔG_{nc} involved in the transformation from one phase to the other must vanish. In the case of the few SMA's which go to an untwinned Martensite it appears that this "ideal" state of affairs may indeed be arbitrarily closely approached in the limit of ever better crystal growing and annealing techniques. In the more usual twinned Martensite case, however, the presence of the twins and associated stressed β , Martensite interface negates this possibility. Therefore, in this case our theory is rigorously applicable only to the stress-strain properties of the material on a scale finer than the intertwin spacing. We will discuss this matter in more detail in Section V. For now we merely state that the theory is applicable to twinning SMA's with only minor elaboration at temperatures well above M_s .

In Sections III and IV we discuss the pre-Martensitic phenomena with particular emphasis on the well studied case of NiTi,² and Section VI addresses the practical potentialities of SMA heat engines. A Glossary is appended at the end of the paper.

II. The Ideal Stress-Strain Diagram

Disregarding ordinary thermal expansion, the single crystal SMA stress-strain diagrams reported by various authors³ have the general appearance schematized in Figure 1. This is the case both with those alloys in which a single crystal of the β -phase transforms to a single untwinned Martensite crystal, and with those in which it transforms to a twinned Martensite structure. At the lowest temperature the internal stresses which cause hysteresis overwhelm the restoring force, and the specimen remains elongated when the external stress is removed. Usually the area of the hysteresis loops

decreases with increasing temperature. There is no question about the "ideal" form of the stress-strain curves at the higher temperatures: First a pure β -phase elastic modulus, then a perfectly flat two phase coexistence region at the transformation stress appropriate to the given temperature and finally, a pure Martensite elastic modulus. Here the transformation is of first thermodynamic order as the two phases are capable of coexisting at equilibrium. Furthermore, the pure Martensite elastic moduli all seem to fall on the same line.

At the lower temperatures at which hysteresis overwhelms the restoring force the situation is less clear, but we reconstruct the full T - ϵ - σ relation of the ideal specimen as being that schematized in Figure 2.

The two coexistence region boundaries come together and end at the critical point which occurs at zero stress and zero strain (i.e., the undistorted β -geometry) and the critical temperature T_c .

This reconstruction may be summed up by three statements:

- 1) Only one phase (Martensite) exists below T_c .
- 2) At a temperature infinitesimally below T_c the geometry of the thermal Martensite is only infinitesimally different from the β geometry, and tends toward a low temperature "limit Martensite geometry" as the temperature is further lowered. Just below T_c the rate of change of the Martensite geometry is most rapid and the restoring force against further stretching the Martensite is very small.
- 3) At a temperature infinitesimally above T_c the geometry of the stress induced Martensite (SIM) at equilibrium with the β -phase is only infinitesimally different from the β geometry, and its rate of change goes to infinity as T_c is approached from above.

Statement 1) is an experimental fact which may be deduced from two observations. First, no such thing as a "stress induced β -phase" exists. Second, it is impossible to produce a supercooled β -phase* by rapid quenching to below T_c . (This is the case with all critical points, and thus directly supports our interpretation.)

* We are aware of the few SMA's in which a supercooled β -phase is obtainable by splat cooling⁴. However, this mode of cooling is so rapid that the resulting β -phase probably has some high temperature disorder frozen into it, and, therefore, is different from the nonquenchable well annealed "equilibrium" β -phase produced by less brutal methods of cooling from the melt which the theory assumes.

Statement 2) appears to have been experimentally verified by the scattering experiments of K. Mukherjee who states: "These results also suggest a progressive cooperative shear and lattice distortion which produces the final Martensite geometry."^{5*}

Statement 3) does not as yet seem to have been verified. However, it is easy to demonstrate that it is sufficient and necessary for the occurrence of the pre-Martensitic phenomena just above T_c . Likewise, statement 2) is necessary and sufficient for their occurrence just below T_c .⁷

III. The Origins of the Pre-Martensitic Phenomena

Figure 2 very much resembles the P-V-T diagram of a single component fluid. (In the fluid case the two phases coexist below T_c rather than above it. This is the usual case but other exceptions are known.)

At the fluid critical point $\left(\frac{\partial P}{\partial V}\right)_T$ goes to zero. This is strictly analogous to $C_{11}-C_{12}$ going to zero in the SMA case. The vanishing of this elastic coefficient causes large amplitude lattice vibrations which are responsible for the well known diffuse diffraction phenomena,² the maximum of internal friction,⁸ and the minimum in the speed of sound.⁹ In the case of the fluid, the vanishing of $\left(\frac{\partial P}{\partial V}\right)_T$ causes critical opalescence (which is strictly analogous to the diffuse diffraction) and the complete absorption of sound.

NiTi exhibits yet another pre-Martensitic phenomenon - a peak in the electrical resistivity upon cooling.^{2, 10} This peak is due to the enhanced scattering of conduction electrons by the large amplitude lattice vibrations in the vicinity of the critical point.

Besides the argument by analogy, there is a deeper one: A higher order

*The temperature dependence of the thermal Martensite geometry somewhat further below T_c is elegantly demonstrated by a simple experiment performed by H. Mohamed of the University of California, Berkeley⁶: A piece of NiTi in the Martensite phase is quasiplastically bent, thereby causing the growth of those Martensite variants whose orientation tends to relieve the applied stress. It is then immersed into liquid nitrogen and spontaneously bends further in the direction of the initial deformation. This further bend is caused by the further change of geometry with decreasing temperature.

phase transition (such as a critical point) occurs whenever a continuous process results in a qualitative change.¹¹ In this case, cooling a specimen which is under zero stress down to infinitesimally below T_C causes an infinitesimal but qualitative change to Martensite symmetry.

IV. Nonideality of Thermal Cycling Under Zero Applied Stress

An ideal specimen would show no hysteresis in any of its properties under thermal cycling. This is not the case with any real specimen and the purpose of this Section is to discuss the origin of this hysteresis for the particular (and best studied) case of zero externally applied stress.

The transformation of an ideal specimen upon cooling under zero stress would be a higher order phase transition in the form of a sudden breaking of cubic symmetry to orthorhombic symmetry at a well defined temperature, followed by further distortion with decreasing temperature. No interface plane would ever form. However, in actual specimens a small amount of Martensite of pronounced orthorhombic form appears at the temperature M_S , and this Martensite grows at the expense of the β phase with well defined interface planes as the temperature is further lowered. The theory states that the transition is of higher thermodynamic order only under rigorously zero stress. Any stress at all causes a transformation to SIM at a temperature somewhat above T_C . Thus, the internal stresses which are inevitable in any real material explain the apparent discrepancy. (We note that the role of these internal stresses is fundamentally different from that of $\Delta G_{nc}^{M \rightarrow P}$ as defined by Tong and Wayman.¹ Rather than impeding the transformation and causing it to require supercooling in order to proceed, they cause it to commence at a higher temperature.)

In the case of NiTi these internal stresses are apparently "worn down" by repeated thermal cycling. This is manifested by a decrease of M_S and a progressively more pronounced resistivity peak on the cooling portion of the cycle.² Sandrock, et.al.² have correlated these phenomena with a microstructural change induced by repeated cycling: A large number of dislocations are seen to form and coalesce in apparently roughly planar tangles. The appearance of these tangles seems to suffice to explain the closer approach to ideality. Within them there are, no doubt, very large local internal stresses and probably numerous Martensite nuclei of many variants even well above T_C . These nuclei are able to grow or shrink and to interconvert by means of twin boundary migration in response to stresses applied from outside

the tangles. We postulate that this allows the tangles to act as "accommodation loci" which concentrate any internal stresses within them, thereby causing the bulk of the material outside of them to be relatively free of internal stresses. As the volume of the tangles is apparently much smaller than the volume of the material between them, this causes the bulk of the specimen to behave more nearly ideally.

As previously stated, supercooling is impossible at a critical point. Internal stresses can and do raise the temperature at which any given region in the material transforms to somewhere above T_C , but they cannot possibly depress the transformation temperature to below T_C . Therefore, in a chemically homogeneous material, $T_C = M_f$, regardless of internal stresses. The reason that the pre-Martensitic phenomena peak at M_S rather than M_f is that below M_S the rapid decrease of the amount of β present with decreasing temperature overwhelms the increase of intensity of the pre-Martensitic phenomena in that portion of the material which is still in the β phase.^{2, 7}

The immutability of M_f is elegantly demonstrated by some as yet unpublished observations of S. Fishman and D. S. Lieberman concerning the behavior of the electrical resistivity of monocrystalline AuCd (49.0 at. % Cd) upon thermal cycling under zero applied stress.¹² They observed that M_S is only a few degrees above M_f and that the cooling curve does not change with thermal cycling. However A_S and A_f , which may be as much as 20° above M_f and M_S , respectively (depending on how long the specimen has previously been held in the Martensite phase) decrease to within a few degrees of M_f and M_S after a number of cycles and remain there upon further uninterrupted cycling. If the cycling is stopped and the specimen is held below M_f for several hours and then resumed, A_S and A_f are found to be at their initial values or even higher. Subsequent continuous cycling again lowers them to within a few degrees of M_f and M_S .

Apparently, in the case of AuCd the internal stresses which raise M_S in NiTi above T_C are not very important, but those which raise A_S above T_C are, and are "worn down" by repeated cycling. However, if the cycling is stopped with the specimen completely in the Martensite phase, there is apparently a microstructural relaxation process which further stabilizes that particular Martensite microstructure. When the specimen is again heated, the thermally induced Martensite is retained as SIM until a certain level of superheating is attained. (In this case the concept of a $\Delta G_{nc}^{M \rightarrow P}$ appears to be perfectly valid. We note that the possibility of superheating under zero stress in no way

contradicts our basic model. Superheating is possible due to the possibility of SIM just as supercooling is impossible due to the impossibility of a stress induced β -phase.)

The change of A_s and A_f of NiTi under thermal cycling is the opposite of that observed in AuCd: As M_s decreases, A_s and A_f tend to increase.¹³ Apparently, in the case of NiTi the microstructural relaxation processes which tend to stabilize the Martensite microstructure are irreversible and not subject to "being worn down". Therefore, the heating portion of the thermal cycle becomes less ideal after a few cycles. Combined with the more nearly ideal behavior on the cooling portion of the cycle this results in a larger area hysteresis loop in the resistivity.

It seems very likely that the same relaxation mechanisms which stabilize a particular Martensite microstructure and thereby increase A_s and A_f upon thermal cycling under zero stress are also responsible for the development of the "two way memory" effect under SMA engine-like cycling which involves straining.¹⁴ The difference between the two cases is that the Martensite microstructure which is formed and stabilized under zero stress cycling is determined by essentially random and accidental internal stresses, while that which is formed and stabilized in the course of SMA engine cycling is determined by the externally applied stresses involved in the engine cycle. The development of the "second memory" in polycrystalline NiTi appears to be irreversible, as a piece of wire which has been "trained" to one engine cycle by several hundred repetitions cannot be retrained to another.¹⁵ This supports our postulate of the essential similarity of the two phenomena.

V. Nonideality in Twinning and Polycrystalline Materials

The main purpose of this Section is to define the limits of validity of our theory when it is applied to SMA's which normally transform to a twinned Martensite and polycrystalline SMA's. As we shall see in the following and final Section, these limitations have important practical implications. The discussion will be framed mostly in terms of the hypothetical SMA heat engine cycles sketched in Figure 3.

For our present purposes, we define ideality as meaning that the microstructure of the specimen at a given e - T point must be independent of the path by which that point is reached. Consider the two paths from point b to point a in Figure 3: $b \rightarrow c$ (critical point) $\rightarrow d \rightarrow a$ involves a higher order phase transition (at the critical point) which does not involve the formation

of an interface plane (in an ideal specimen) and, thereby, results in an untwinned Martensite at d. Upon heating up to a, this Martensite partially reverts to β and, since the remaining Martensite is untwinned a very highly stressed interface plane results. b \rightarrow a, however, is simply a partial stress transformation to twinned SIM and results in an interface plane which is only mildly stressed. Therefore, we are forced to conclude that the assumption of ideal behavior in the twinning Martensite case is logically inconsistent with itself, as it leads to a prediction of a nonsingly defined T - ϵ - σ relationship.* Although the precise mechanism invoked here is unlikely to occur in a real specimen, the thought experiment suffices to establish the principle. A similar argument applies to the cycle a, b, c', d'.

We now turn to the hypothetical engine cycle e, f, g, h and consider the two alternate paths between f and e, f \rightarrow e and f \rightarrow g \rightarrow h \rightarrow e. Here both f \rightarrow e and g \rightarrow h result in a two phase structure involving a twinned Martensite and an interface plane. Heating (and slightly stretching) to get from h to e results in nothing more than a slight additional elastic distortion of both phases. If the elastic moduli of the two phases are roughly the same (which generally appears to be the case), this slight additional elastic deformation clearly transforms the strain accommodation dictated structure which is optimal at h to that which is optimal at e. Thus we see that SMA engine cycles which are completely well above T_c may selfconsistently be imagined to progress in an ideal manner as long as detwinning does not occur.

Single crystals of a few SMA's have actually been observed to behave nearly ideally well above T_c .³ In agreement with the present theory, the areas of the isothermal stress-strain hysteresis loops tend to increase as the temperature is lowered.

We now turn our attention to the most interesting case of all - that of a polycrystalline specimen of a twinning SMA. (We will continue to refer to Figure 3 although we recognize that the T - ϵ - σ relationship of a near-ideal polycrystalline material would be somewhat different. This difference is not great enough to invalidate the succeeding arguments.)

As in the monocrystalline case, the only fundamental nonideality intrinsic in the cycle e, f, g, h is the possibility of detwinning. Actually, it appears

*Although it is possible to imagine relaxation processes which "close the cycle", these processes appear likely to be so slow that their possible occurrence is irrelevant to all but the most rarified theoretical speculation.

that detwinning is not a very serious problem in polycrystalline materials. This is because the deformation of polycrystalline Martensite seems to occur via Martensite plate tapering rather than by massive twin plane migration.¹⁴ While the portion of a given Martensite plate in the interior of a subgrain tapers in response to applied stress, the edges of its boundary planes remain firmly fixed at the subgrain boundaries.

We now turn to the cycle a, b, c, d in the polycrystalline case. The nonideality mechanism which we postulated above for the monocrystalline twinned Martensite case is actually unlikely to be very important if the material possesses a good "second memory" as it must after having been carried through the cycle a number of times. If it possesses a good second memory, the Martensite microstructure attained by cooling from b to d must strongly resemble that which is optimal at a and, thereby, convert to that at a upon heating. Therefore, the initially postulated source of nonideality is unlikely to be very important. However, by the very nature of the "second memory" this Martensite microstructure is inordinately stabilized by "non-chemical free energy". Therefore, the partial reversion to the β -phase which is necessary to obtain the microstructure which is optimal at a can be achieved only with some degree of superheating. Thus, we see that the nonideality removed by "double training" is replaced by another sort which is implicit in the dual memory phenomenon. Again, a similar argument applies to the cycle a, b, c', d'. If the second memory is actually imperfect, yet a third source of nonideality arises: Upon cooling through the critical point, some regions of the material transform to twinned "supervariants" which are not those optimal at a. Therefore, stretching from c to d requires the application of stress which, ideally, it should not. Also, if some regions of "inappropriate supervariant" are retained at d and, hence, at a, they will not exert the optimal reversion stress on the "power stroke" a \rightarrow b. The first and third of these postulated nonideality mechanisms seem sufficient to account for the large discrepancy between the flow (b \rightarrow a) and reversion stresses typical of "virgin" NiTi.

We have not at all discussed the pronounced stress-strain hysteresis of polycrystalline SMA's even well above T_c which are, no doubt, due to the

effects of the grain boundaries. All we can say at this time is that we have been unable to find any fundamental reason that this hysteresis should be inevitable, and hope that improved metallurgical technique will succeed in minimizing it.

VI. Potential SMA Engine Efficiency and Output

The fundamental thermodynamic prerequisite for a heat engine to be (at least theoretically) capable of attaining the Carnot efficiency is that its working material be thermodynamically ideal. If the working material is nonideal, the potential thermal efficiency of an engine can only decrease for, if it were to increase, it would be possible to construct a device which would violate the Second Law of Thermodynamics.

Therefore, it behooves the engine designer to use as nearly ideal of a working material as possible, and to confine the engine cycle to that portion of the material's T - ϵ - σ diagram in which the deviations from ideality are as small as possible. As we have seen, those engine cycles of twinning SMA's which go below or come close to T_c are fundamentally incapable of approaching ideal behavior. However, as long as detwinning does not occur, these difficulties do not arise with engine cycles which are completely well above T_c . Hence, this latter category of cycles is thermodynamically more desirable. Another, purely practical, reason for staying away from the critical point is that the large heat capacity peak there would make a thermodynamically efficient engine difficult to design.

The SMA engine community seems to have been fixiated upon engine cycles which go below T_c and utilize the shape memory effect simply because the SME is the most spectacular property of these materials. However, the SME is not necessary for heat engine operation; all that is really necessary is that the stress-strain curves be strongly dependent on temperature, and this requirement is amply fulfilled by the strong parallel temperature dependence of the flow and reversion stresses.

Reversion and irreversible plastic flow stress data for polycrystalline NiTi recently presented by Perkins, et.al.¹³ indicates that work outputs of up to about 1.0 - 1.5 j/g/cycle should be attainable with existing or slightly improved NiTi. At 60 rpm (which is typical of existing prototypes) this is equivalent to a respectable 1.0 - 1.5 kw/kg. The potential work output per cycle is ultimately limited only by irreversible damage under the most extreme conditions of temperature and stress encountered during the cycle.

This and nonideality seem to be the prime metallurgical problems which must be addressed.

Acknowledgements

Many thanks for numerous spirited and stimulating discussions to Professor David S. Lieberman who largely inspired the painstaking analysis of Sections IV and V. Also, thanks to Ridgway Banks for first bringing Nitinol into the Lab and, thereby, to my attention. May his engine live to see its 10^8 th cycle (which it probably will). I would also like to thank Mr. Jack Williams for assistance in the preparation of the manuscript, and Rob Ritchie and Noel Kennon for their valuable comments.

This work was supported in full by the U. S. Energy Research and Development Administration.

Glossary

Where possible, we have adhered to the standard terminology of the shape memory alloy literature (in as far as it is defined) and the standard terminology of classical thermodynamics. Neologisms are indicated by an asterisk(*) and non-standard definitions by a dagger (+). We have included this admittedly lengthy glossary because this paper is intended for two distinct groups of readers with markedly different backgrounds and scientific vocabularies.

A_s, A_f . Two empirically defined temperatures. When a specimen which is initially in the Martensite phase is heated up, the first visible traces of Austenite (or β -phase) appear at A_s , and the last visible traces of Martensite transform at A_f . When stress is not specified, zero stress is usually assumed. $A_f \geq A_s \geq M_f \approx T_c$. Also, $A_f \geq M_s$.

Austenite. In this context, synonymous with β -phase.

β -phase or β . That SMA phase which is thermodynamically stable at $T > T_c$ and zero stress. In most cases, CsCl structure.

$C_{11}-C_{12}$. Standard notation for that elastic constant of the β phase which decreases

with decreasing temperature and finally vanishes at T_c (i.e., at the critical point).

Critical phenomena. Various physical phenomena caused by the divergence of compliance coefficients in the vicinity of a critical point. Typically, large fluctuations of various sorts and a large heat capacity maximum.

Critical point. A point in thermodynamic variable space at which two coexisting phases become identical. (See Ref. 16 or the discussion in any equivalent text.)

Critical temperature or T_c . The temperature at which a critical point occurs. (In the SMA case, strongly dependent on chemical composition.)

Detwinning. The mutual annihilation of parallel twin planes which have been forced together by externally applied stresses.

Double training^{*}. The process by means of which a second memory is imprinted on a specimen of SMA. (Typically, many repetitions of a heat engine cycle.)

Equilibrium stress^{*}. In reference to an ideal specimen at a given $T > T_c$: The value of tensile stress at which Martensite and β can coexist in equilibrium.

First order phase transition. A type of phase transition at which all thermodynamic functions except the free energy are discontinuous. In the present context, stress transformation.

Flow stress. In reference to isothermal tensile test: Stress required to stretch specimen an infinitesimal bit more. Function of temperature and strain. In the case of ideal specimen at $T > T_c$, same as equilibrium stress. (c.f. Ref. 13)

ΔG_{nc} or $\Delta G_{nc}^{M \rightarrow P}$. See non-chemical free energy.

Higher order phase transition. A phase transition at which the energy and entropy are continuous. However, their higher derivatives are generally discontinuous and often diverge. In the present context, a critical point. (Often called second order phase transition, but this term is archaic and, in most cases, incorrect.)

Ideal^{*}. Capable of transversing any thermodynamic path completely reversibly in the limit of an infinitesimally slow (quasi-static) process. Classical thermodynamics is directly applicable only to hypothetical ideal materials.

Interface plane. The plane separating the Martensite and β -phases when they coexist at equilibrium within a single crystal. See also monocrystalline and strain accommodation.

Limit Martensite geometry^{*}. Refers to the limit $T = 0$ under zero stress.

M_s , M_f . Two empirically defined temperatures. When a specimen of SMA which is initially completely in the β -phase is cooled, the first visible traces of Martensite appear at M_s , and the last visible traces of β -phase transform at M_f . $A_f \geq M_s \geq M_f \approx T_c$.

Martensite. SMA phase which is thermodynamically stable at $T < T_c$, regardless of stress. May also be made at $T > T_c$ by applying stress to β -phase. Non-simple orthorhombic structure in most or all cases.

Martensite microstructure[†]. The detailed microstructure (definition including the distribution of variants and twin planes) of a specimen in the Martensite phase. Also applied to β -phase or mixed phase specimens in the sense of the detailed microstructures they would have if completely transformed to Martensite by cooling. Occasionally used by us in specific reference to those microstructural details which determine the second memory shape. See also two way memory.

Monocrystalline[†] and single crystal[†]. In our usage, any specimen of SMA which may be converted to a single crystal of β -phase by heating to $T > A_f$.

Non-chemical free energy or ΔG_{nc} or $\Delta G_{nc}^{M \rightarrow P}$. That portion of the free energy change involved in the transformation from one SMA phase to the other which is due to the effects on nonidealities such as the presence of a stressed interface plane and dislocations. Superscript M \rightarrow P indicates that the Martensite to β transformation is meant. (c.f. Ref. 1)

Non-twinning[†]. In our usage, any SMA which transforms from the β -phase to an untwinned Martensite upon cooling.

Orthorhombic[†]. In our usage, any structure of orthorhombic symmetry; i.e., not necessarily simple or face-centered orthorhombic.

Polycrystalline[†]. See mono-crystalline.

Pre-Martensitic phenomena. Various critical phenomena observed near the SMA critical point. Generally in reference to $T > M_s$.

Quasi-plastic deformation. Deformation of twinned Martensite structure by the mechanism of twin boundary migration. "Quasi" because heating the specimen to $T > A_f$ transforms the specimen to the β -phase in which the twin planes become mirror planes and, therefore, the deformation is undone. See also shape memory effect.

Restoring force^{*}. In reference to tensile test. Force with which a specimen pulls on the grips when the specimen is allowed to slowly contract. Same as equilibrium stress in the case of an ideal specimen at $T > T_c$.

Reversion stress. Restoring force in an experiment in which a specimen initially in the Martensite phase is quasiplastically deformed, clamped, and heated up to $T > A_s$ at constant strain. (c.f. Ref. 13) Same as equilibrium stress in the case of an ideal specimen.

Second memory. See two way memory.

Second order phase transition. See higher order phase transition.

Shape memory alloy or SMA. An alloy which exhibits the shape memory effect.

Shape memory effect or SME. A specimen of SMA in the Martensite phase is quasiplastically deformed at $T < T_c$. When heated up to $T > A_f$, it returns the shape that was originally imprinted on it by high temperature annealing and exerts considerable force in doing so.

Strain accomodation. In reference to the coexistence of Martensite and β -phase within a single macroscopic crystal. The two lattices fit together coherently on the macroscopic scale, thereby minimizing the interfacial strain energy. In

most cases, this fit is rendered possible in part or in whole by the presence of numerous parallel twin planes in the Martensite phase. (c.f. Ref. 17) In many cases, periodic stacking faults also figure in the strain accommodation mechanism.

Stress induced Martensite or SIM. Name arbitrarily given to Martensite phase made by stressing β -phase at $T > T_c$. See also thermal Martensite.

Stress transformation or stress induced transformation. The transformation of β -phase to SIM.

Supervariant^{*}. In the case of most SMA's, a single crystal of β -phase may transform to any one of 24 crystallographically equivalent twinned Martensite structures, each consisting of alternating domains of two Martensite variants separated by parallel twin planes. (See Ref. 17.) We refer to these 24 possible twinned structures as supervariants.

T_c ^{*}. Critical temperature, temperature at the critical point.

T_0 [†]. In reference to an ideal specimen at $T > T_c$. For a given externally applied stress, the temperature at which the two phases coexist at equilibrium. Often used to indicate the equilibrium temperature under zero applied stress, in which case T_c is actually meant.

Thermal Martensite. Name arbitrarily given to Martensite phase formed by cooling β -phase to $T < T_c$ under zero applied stress. In case of ideal specimen and probably also in most actual cases, thermal Martensite bears the same thermodynamic relation to SIM as supercritical steam bears to subcritical steam; i.e., they are the same phase under different conditions of temperature and stress.

Transformation stress. At a given $T > A_f$, the stress at which β -phase transforms to SIM. In the case of an ideal specimen, same as equilibrium stress.

Twin plane. A type of lattice defect. In the simplest case, the lattice on one side of a twin plane is an exact mirror image of the lattice on the other side.

Twinning[†]. In reference to those SMA's whose Martensite phase is ordinarily twinned.

Two way memory. After an SMA specimen has been put through a large number of heat engine cycles, it typically develops a second memory; i.e., when it is cooled to below T_c under zero applied stress, it spontaneously deforms to that shape to which the engine has been deforming it in the course of cycling.

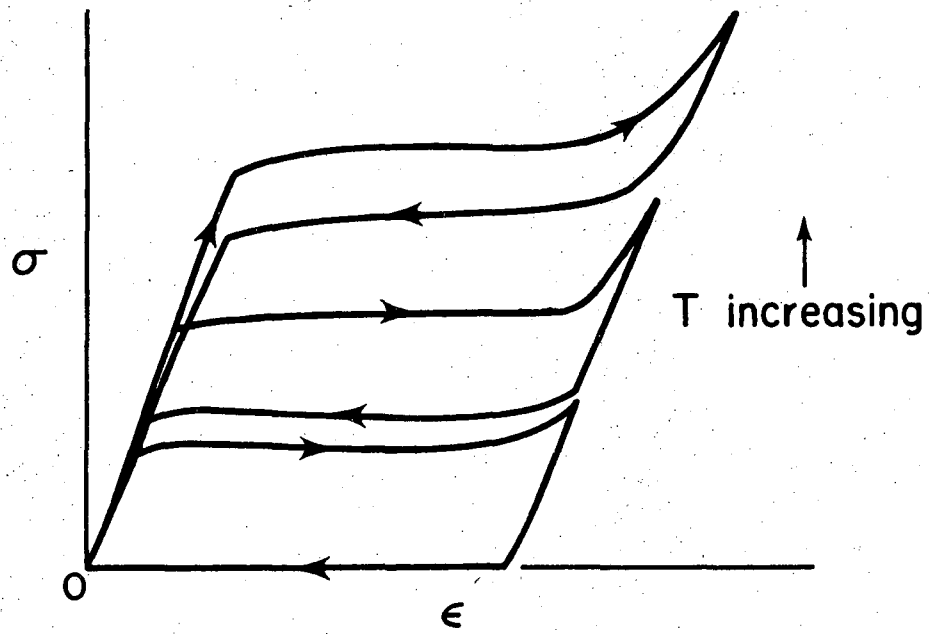
Variant. In the case of a hypothetical homogeneous transformation, a cubic lattice could deform to any one of six equivalent orthorhombic lattices which are referred to as the six Martensite variants.

References

1. H. C. Tong and C. M. Wayman, *Acta. Met.* 22, 887 (1974), 23, 209 (1975).
2. G. D. Sandrock, A. J. Perkins and R. F. Hehemann, *Met. Trans.* 2, 2769 (1971).
3. H. Pops, *Met. Trans.*, 1, 251 (1970), R. V. Krishnan and L. C. Brown, *Ibid.*, 4, 423 (1973), C. Rodriguez and L. C. Brown, in Shape Memory Effects in Alloys, A. J. Perkins, ed., Plenum Press (New York, 1975, in press).
4. H. Warlimont and L. Delaey, Martensitic Transformations in Copper-Silver- and Gold-Based Alloys, *Prog. Mat. Sci.* 18, Pergamon Press (Oxford, 1974) pp. 5-6.
5. K. Mukherjee, in Shape Memory Effects in Alloys.
6. H. Mohamed, private communication, Berkeley, 1975.
7. S. Vatanayon and R. F. Hehemann, in Shape Memory Effects in Alloys.
8. C. M. Jackson, H. J. Wagner and R. J. Wasilewski, 55 - Nitinol - The Alloy with a Memory: Its Physical Metallurgy, Properties, and Applications, Report NASA-SP5110, Technology Utilization Office, NASA (Washington, 1972) pp. 39-42.
9. *Ibid.*, pp. 30-35.
10. *Ibid.*, pp. 23-31.
11. L. D. Landau and E. M. Lifshitz, Statistical Physics, Addison-Wesley Publishing Company, Inc. (Reading, 1958) pp. 430-456.
12. D. S. Lieberman, private communication, Berkeley, 1975.
13. Jeff Perkins, G. R. Edwards, C. R. Such, J. M. Johnson and R. R. Allen, in Shape Memory Effects in Alloys.
14. L. Delaey, R. V. Krishnan, H. Tas and H. Warlimont, *J. Mat. Sci.* 9, 1521 (1974).
15. A. D. Johnson, LBL, private communication, 1975.
16. H. B. Callen, Thermodynamics, John Wiley & Sons, Inc. (New York, 1960) Ch. 9.
17. D. S. Lieberman, M. S. Wechsler and T. A. Read, *J. Appl. Physics* 26, 473 (1955).

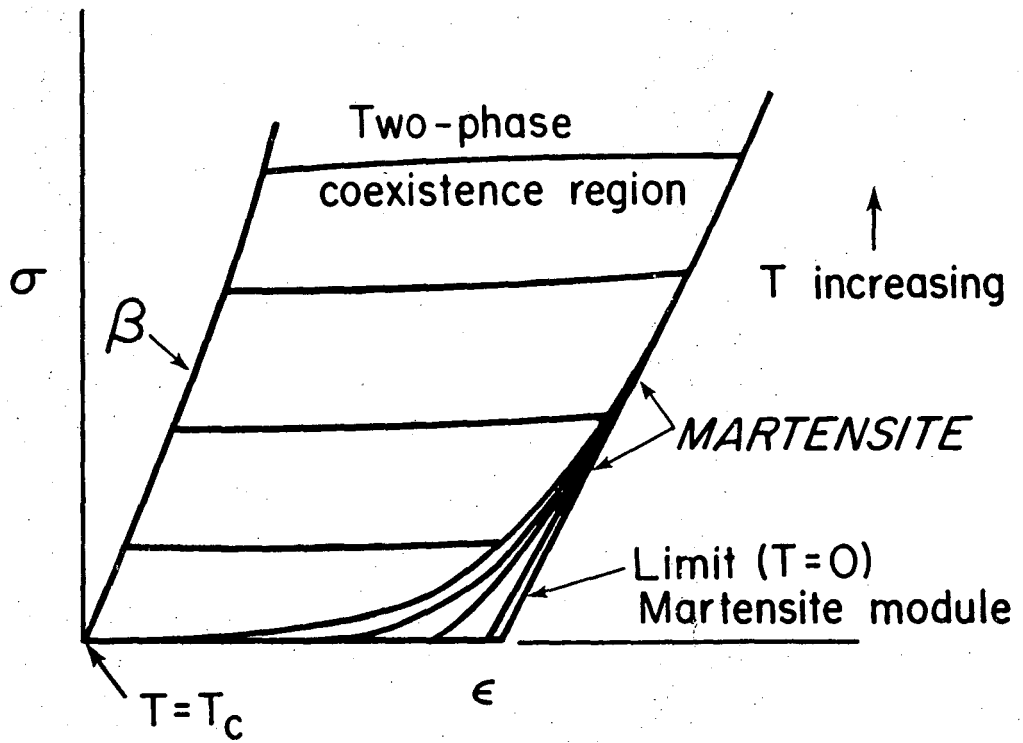
Figure Captions

- Figure 1. Schematized stress-strain curves of a single crystal of SMA under tensile stress. (Ordinary thermal expansion has been disregarded.).
- Figure 2. The stress-strain properties of an ideal single crystal of SMA. (Based on Figure 1.).
- Figure 3. Hypothetical SMA heat engine cycles discussed in text.



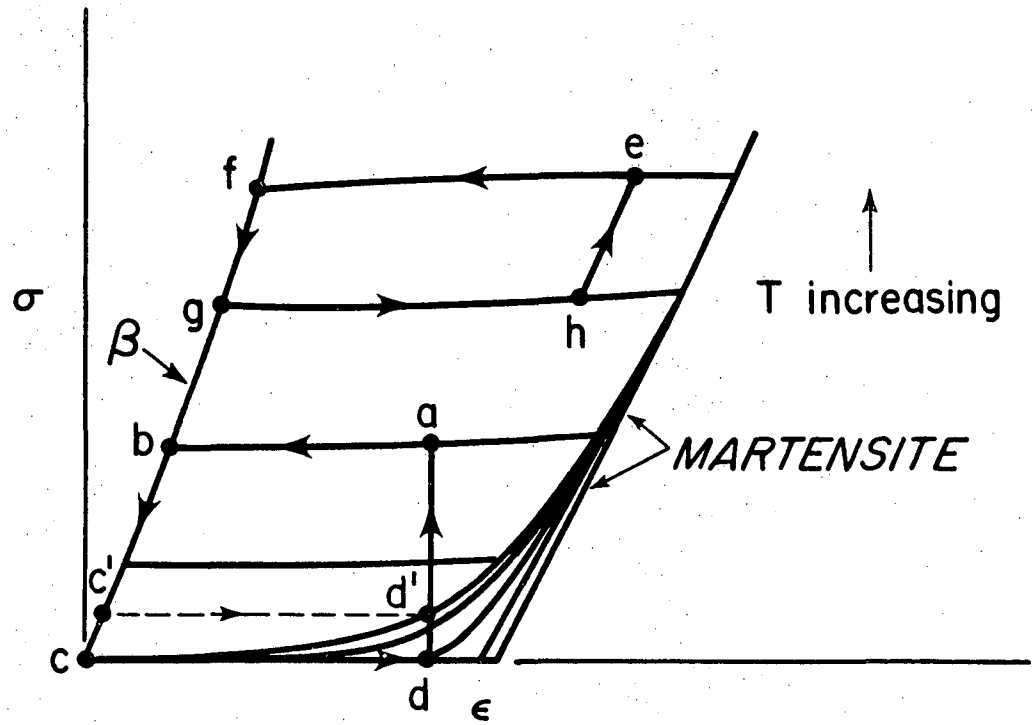
XBL 758-3673

Fig. 1



XBL 758-3674

Fig. 2



XBL 759-3893

Fig. 3

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720