

Review

Thermoelasticity, pseudoelasticity and the memory effects associated with martensitic transformations

Part 1 *Structural and microstructural changes associated with the transformations*

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The literature pertaining to the microstructural and crystallographic features of thermoelasticity, pseudoelasticity and memory effects associated with martensitic transformations is reviewed. The interrelations between the various effects are described. An introduction to the mechanical behaviour and the thermodynamic parameters is given.

1. Introduction

Martensitic transformations can be induced by the application of stress as well as by changes in temperature. This interchangeability of temperature and stress as variables affecting the transformation is due to two effects:

(1) the free enthalpy of the matrix and product phase and thus their equilibria depend not only on variations in temperature and composition but also on stress (the influence of shear stresses is dominant; volume stresses become significant only in the ultra-high pressure range e.g. [1]);

(2) the nucleation and growth processes are associated with shear strains and these will interact with stresses acting within, or applied to, the specimen.

Moreover, the thermodynamic (1) and the kinetic (2) effects are strongly dependent on the directions of stresses with respect to the lattice orientations. This nature of martensitic transformation leads to the effects which are treated on their common basis in this paper: thermoelasticity, pseudoelasticity, the shape memory

effect and the two-way shape memory effect. Our main goal is to compile experimental and theoretical results thus far obtained in this field and to relate the various phenomena to the principal properties associated with martensitic transformations.

First we shall describe briefly the transformation and the deformation phenomena which will be treated.

A *thermoelastic martensitic transformation* is realized if martensite forms and grows continuously as the temperature is lowered, and shrinks and vanishes continuously as the temperature is raised as shown in Fig. 1. Fig. 2a gives a schematic representation of this transformation by indicating the increase in internal stresses, σ_1 (and, thus, of stored elastic energy) and the fractional increase in the amount of martensite as measures of the progress of transformation, and the decrease of these properties due to the reverse transformation. There is no sudden appearance or disappearance of large groups of plates (burst). The trans-

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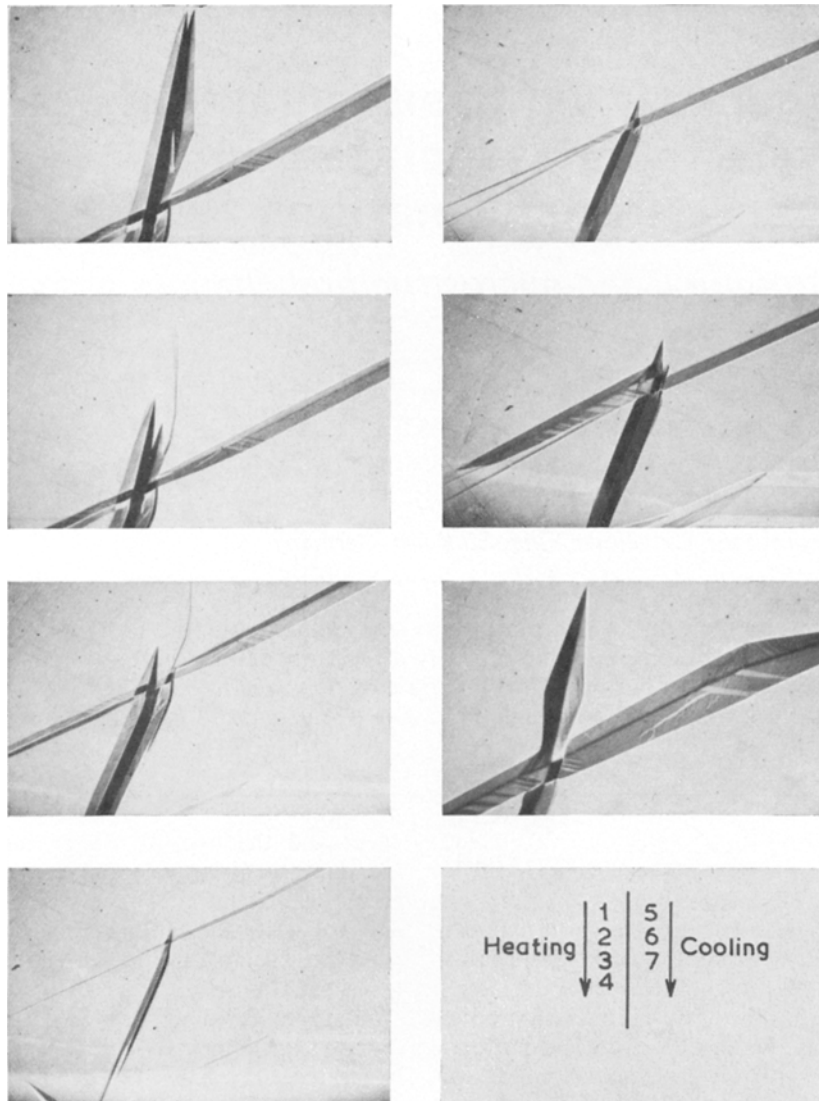


Figure 1 Thermoelastic behaviour in AgCd showing the growth of self-accommodating groups.

formation proceeds essentially in equilibrium between the *chemical driving energy* of the transformation and a *resistive energy* whose dominating component is the stored elastic energy. Thus the transformation is defined as being *elastic* or *degenerate elastic* if during the growth process the chemical driving energy is always in equilibrium with the resistive energy. The term *degenerate elastic transformation* refers to a process which shows small local discontinuities or jumps during the growth of a martensite plate. The transformation is said to be *spontaneous* or *burst* whenever the chemical driving energy exceeds the resistive energy to a great extent. Once the transformation starts, the growth or catalytic nucleation cannot be suppressed by external influences.

The *pseudoelastic behaviour* is a complete mechanical analogue to the thermoelastic transformation. In this case the transformation proceeds continuously with increasing applied stress, σ_a (and external strain ϵ) and is reversed continuously when the stress is decreased. Fig. 3 shows an example of this behaviour in terms of a

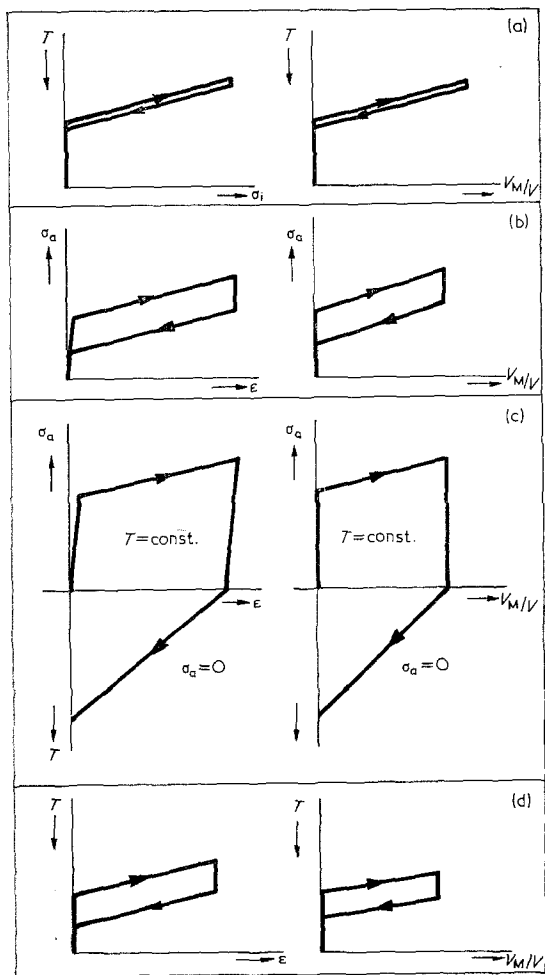


Figure 2 (a) Schematic representation of the formation and reverse transformation of thermoelastic martensite as a function of temperature; σ_i represents the internal stresses arising by the transformation, V_M/V the fractional volume of the martensite product. (b) Schematic representation of pseudoelasticity. Martensite forms as the applied stress is increased producing the macroscopic strain. Release of stress causes the martensite to revert to the parent phase. (c) Schematic representation of shape memory effect. Martensite is formed by straining but remains stable upon removal of the external stress; it is reverted to the parent phase on heating. (d) Schematic representation of two-way memory effect. On cooling macroscopic strain is produced without the application of an external stress; the strain disappears again on increasing the temperature.

stress-strain curve. The "plastic" strain is caused by the shape strain accompanying the formation of martensite. Therefore, recovery occurs when the transformation is reversed. In

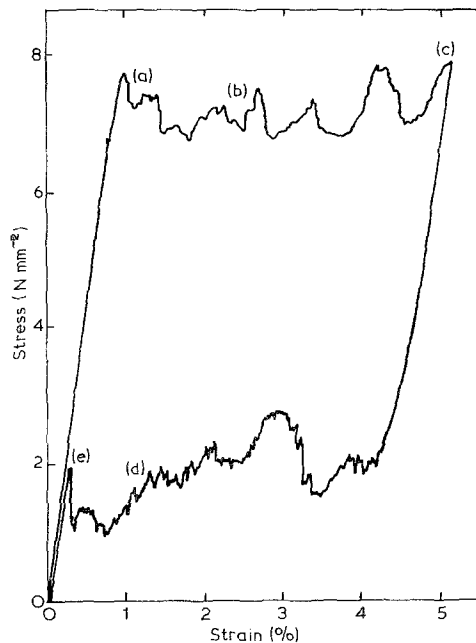


Figure 3 Tensile curve showing the pseudoelasticity in a Ag-Cd alloy. The upper part of the curve corresponds to the transformation, the lower part corresponds to the reverse transformation. The letters on the figure correspond with the microstructures given in Fig. 6 [30].

the left-hand diagram of Fig. 2b the stress-strain curve of Fig. 3 is drawn schematically whereas the diagram on the right in Fig. 2b indicates the concomitant change in fractional martensite volume. It will be noted that in Fig. 2b a hysteresis is shown to occur. This behaviour is due to the interaction of several thermodynamic and kinetic factors. The treatment of these with respect to all phenomena of present interest is the subject of Part 3 of this series.

The *shape memory effect* arises if a macroscopic deformation is accompanied, as before, by a martensitic transformation which is not reversed by removing the applied stress; in a second step the reverse transformation and a concomitant reversal of the macroscopic deformation are induced by heating. An example is shown in Fig. 4. Fig. 2c shows this behaviour schematically; the left-hand diagram pertains to the performance of a shape memory experiment in a tensile test. The upper half represents the response of the specimen to the isothermal increase and decrease of the applied stress, the lower half to the effect of the subsequent temperature increase. The right-hand diagram

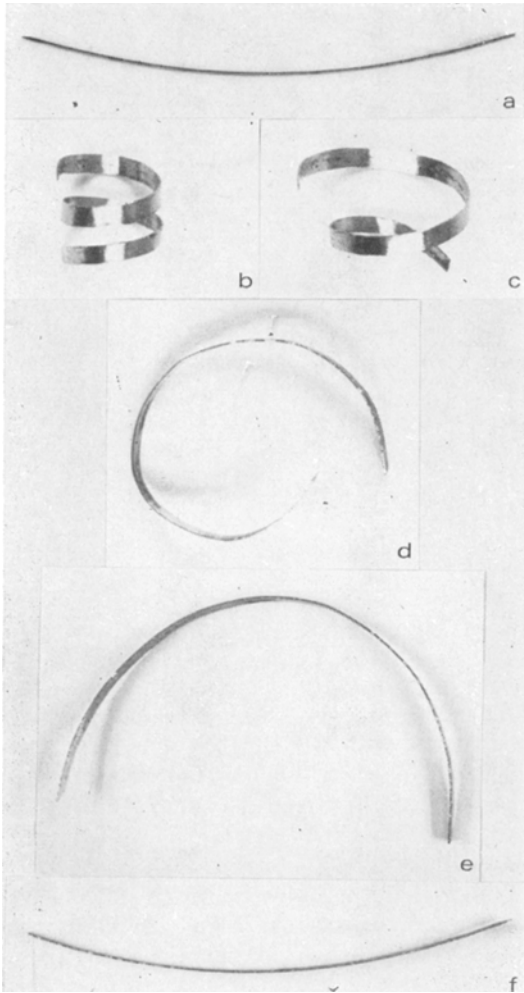


Figure 4 (a) A series of photographs showing the shape memory effect (a) the undeformed state, (b) after deformation and before the shape recovery, (c), (d) and (e) during the shape recovery, (f) after the shape recovery has been completed.

indicates the change in fractional amount of martensite again.

The idealized curves of Fig. 2a to c indicate that close interrelations of the processes exist. It will be recognized that if the hysteresis in the case of pseudoelastic transformation is so large that the reverse transformation is incomplete at $\sigma_a = 0$, the residual martensite can be reverted by heating, i.e. by employing the shape memory effect. This exhibits the interchangeability of stress and temperature as state variables. Thermodynamically the relation is given by the Clausius-Clapeyron equation in a form modified

to account for shear strain as well as volume changes. Treatments of martensitic transformations on this basis are not new. They have been employed to compute the transformation enthalpy from the changes in transformation temperatures (both forward and reverse) with applied stress [2, 3].

Up to this point we have implied that pseudoelasticity and the shape memory effect were associated with a martensitic transformation. The same phenomena can occur even when the specimen is fully martensitic at the outset. In this case the reversible fraction of the resistive energy is stored by *reorientation* of the martensite plates and/or their internal structure (e.g. twins). Thus, pseudoelasticity and the shape memory effect may be associated with a martensitic transformation, a reorientation of a martensitic structure or a combination of both.

The final process to be described is the *two-way shape memory effect* (Fig. 2d). This term refers to a reversible shape change accompanying thermally induced martensite formation and reverse transformation. Normally, a thermal martensitic transformation proceeds by the formation of random numbers of martensite plates of each orientation variant in a sufficiently large sample such that no macroscopic shape change occurs apart from a volume change. In the case of a preferred orientation distribution of nuclei the transformation leads to a corresponding limitation of orientation variants which, in turn, causes an anisotropic macroscopic shape change. If the nuclei are not destroyed upon reverse transformation or by high-temperature annealing, the transformation-induced shape change can be repeated through successive thermal cycles. An extreme example of the two-way shape memory effect is the reversible shape change accompanying a single interface martensitic transformation due to the presence of only one nucleus. However, preferred orientations of persistent nuclei can, also, be induced by plastic deformation of the matrix, of the martensite or by inducing the first transformation under uniaxially applied stress.

The martensitic transformations and the reorientation of martensitic structures by applied stresses may be treated as deformation processes which are closely related to twinning. The treatment of continual mechanical twinning by Bolling and Richman [4] taking into account a free energy change is, in fact, identical to a treatment of the growth process of a diffusionless

structural transformation under stress as Laves has pointed out [5]. Its application to martensitic transformations in Fe–Ni–C alloys [6] has shown its potential. In the present papers a treatment on this general basis, but with extended attention to structural details, leads to a more complete assessment of the interactions of stress with martensitic transformations.

The shape memory effect and the other processes discussed are not recent discoveries. The continuous appearance and disappearance of martensite with falling and rising temperature, i.e. the thermoelastic behaviour, has been observed by Greninger and Mooradian in a Cu–Zn alloy as early as 1938 [7], but the first detailed study of this effect was only published 11 years later by Kurdymov and Khandros [8]. Pseudoelasticity and the shape memory effect were implicitly studied by observations of length changes by temperature variation and concomitant martensitic transformation under constant load by Scheil in Fe–Ni alloys [9] and by Hornbogen and Wassermann in Cu–Zn [10]. The shape memory effect was also observed in AuCd by Chang and Read [11]. Pseudoelasticity due to reorientation and transformation was recognized by Burkart and Read in In–Ti [2] and by Chang and Read in AuCd [11] and was studied extensively by Birnbaum and Read [12]. The recent revival of interest in the shape memory effect was instigated by the investigations on NiTi by Buehler and co-workers (e.g. [13]) who also observed the two-way memory effect. Although Wang and his associates assume that the structural transitions in this alloy are unique [14, 15] all essential features of present interest (in NiTi) correspond to those of the other alloys as shown, in particular, by the extensive work on NiTi by Wasilewski [16] and Nagasawa [17, 18].

In Table I we have compiled the alloy systems and phases which have so far been investigated with respect to one or more of the effects covered in the present paper. The dominant role played by bcc β -phases, as the parent phase, will be noted. This is due to distinct and comparatively large thermodynamic differences between the transformations of β -phases as compared, for instance, with the fcc \rightarrow bcc (bct) transformations in ferrous alloys.

Several previous papers have dealt with the principles which govern the interactions of stresses with martensitic transformations. Much of this review is based on work by Nagasawa [18], Nakanashi *et al.* [19], Pops [20], Tas *et al.* [21],

Warlimont and Delaey [22], Wasilewski [16], Wayman and Shimizu [23], Perkins [24], Bolling and Richman [4, 6] and Nakanishi [25]. Since a number of different terms are in use for the phenomena of present interest, Table II gives a survey of the terminology, corresponding terms being grouped together.

The following section deals with the structural basis and the microstructural changes associated with the transformations. In Part 2 the macroscopic mechanical behaviour and its characteristic variables are described. Part 3 deals with the thermodynamics and kinetics of the processes. Some of the open questions will also be discussed and considerations regarding practical applications of these effects summarized.

2. Structural and microstructural changes associated with the transformations

The formation of a martensite plate is accompanied by a macroscopic shape change. Although martensite formation is associated with this shape change which is characterized by an invariant plane strain minimizing the two-dimensional strain along the habit plane (plane AB in Fig. 5a), a three-dimensional strain is built up as the martensite plate grows into the third dimension. If the transformation occurs in a single crystal and if the habit plane extends from one free surface to the other free surface (Fig. 5a), i.e. a single-interface transformation, the two ends of the parent will be displaced with respect to each other. The amount and direction of the displacement will result from the thickness and relative orientation of the martensite plate. The formation of this single martensite plate can occur on cooling or on applying an external stress to the single crystal. The examples known in the literature are single-interface transformations upon cooling AuCd [26] and In–Ti single crystals [27] and Fe whiskers [28]. Examples of a single interface transformation by deformation are known for Cu–Al–Ni [29] and Ag–Cd [30] (Fig. 6). Upon heating the crystal or upon releasing the stress, the martensite plate may disappear by the same martensitic mechanism. The original shape of the crystal will be restored. Thus the single interface transformation which occurs during alternating cooling and heating or loading and unloading demonstrates the simplest mechanism for obtaining the two-way memory effect and pseudoelasticity.

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