6. L. A. TANOVIC, J. L. WHITTON, G. CARTER, M. J. NOBES and J. S. WILLIAMS, Proceedings of the VII International Conference on Atomic Collisions in Solids, Moscow (1977) to be published.
7. D. J. BARBER, F. C. FRANK, M. MOSS, J. W. STEEDS and I. S. T. TSONG, *J. Mater. Sci.* 8 (1973) 1030.

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Determination of the recovery stresses developed by shape memory alloys

The mechanical shape memory effect is exhibited by several alloys, all of which undergo thermo-elastic martensitic transformation [1]. The memory effect is demonstrated by inducing a macroscopic strain within a certain range in a specimen while in the martensitic state, and then heating to revert martensite to the high temperature phase (HTP). During reversion, the specimen tends to recover its original unstrained shape. Strain recovery starts at the A_s temperature and finishes at the A_f temperature*.

One of the most interesting applications of shape memory alloys is in energy conversion devices that utilize the memory effect in converting low grade heat sources into useful mechanical work [2–4]. In evaluating the performance of a particular alloy in such devices it becomes essential to determine the levels of recovery stresses† developed during the martensite → HTP transformation upon heating. There have been a few investigations dealing with experimental measurements of the recovery stresses developed by Ni–Ti alloy near the equi-atomic composition [5, 6]. However, no attempt has been made as yet to predict these stresses. In the present paper, a simple relationship has been developed between the recovery stresses, temperature and strain.

For the discussions which follow, it is instructive to identify a reference point from which the macroscopic strain is measured i.e., a zero-point strain. This can conveniently be taken to be the point at which the material consists entirely of the HTP.

Consider a polycrystalline shape memory alloy that has been almost entirely transformed to martensite by cooling it to a temperature at or below its respective martensite finish temperature M_f. In the absence of an external or appreciable internal stresses, all the martensite variants that are crystallographically equivalent would form with equal probability. Therefore, no net macroscopic strain as measured from the zero-point would be expected, and hence no recovery stresses would develop during the reverse transformation to the HTP. In order to realize a recovery stress, the material must acquire a macroscopic strain relative to the zero-point. In terms of the microstructural features, this corresponds to a certain degree of directionality in the distribution of the martensite variants throughout the microstructure. It has been shown experimentally that any strain within the recoverable range is accommodated by reorientation of a volume fraction of the thermally induced martensite [7–10]. This occurs by preferential growth of the most favourably oriented martensite variants. It is then expected that the recovery stress, σ_r, would be proportional to the volume fraction of re-oriented martensite (V_M). This determines the functional dependence of σ_r, on strain ϵ.

Upon heating to within the A_s–A_f temperature range a certain volume fraction of martensite tends to revert to the HTP. The driving force for such reversion arises from the chemical free energy difference between the two respective structures, the elastic strain energy stored in the lattic during the transformation to martensite and energy associated with reversible defects, e.g., twins. As the temperature increases within the range A_s–A_f,

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* A_s = temperature at which the martensite → HTP transformation starts during heating.

A_f = temperature at which this transformation finishes during heating.

† A recovery stress is defined as the external stress required to balance the internal stresses that tend to revert martensite to the HTP.

the driving force increases and in turn the volume fraction of martensite that tends to revert to the HTP (V_{HTP}).

It follows that σ_r increases as V_{HTP} increases with temperature. This determines the functional dependence of σ_r on temperature within the range A_s–A_f.

It can be concluded from the above discussion that:

$$\sigma_r \propto V_{HTP}(T) \cdot V_M(\epsilon) \qquad (1)$$

σ_r would be limited by the minimum stress required to initiate irreversible plastic deformation in the martensite structure and/or the HTP. The yield stresses of the HTP are, however, expected to be lower than those of the martensite due to (i) the lower symmetry of the martensite structure and (ii) the finer grain size of the martensite phase. Therefore, the proportionality constant in Equation 1 can be taken to be the yield stress of the HTP, σ_Y^{HTP}, that is consistent with the state of temperature and strain and hence,

$$\sigma_r = \sigma_Y^{HTP} \cdot V_{HTP}(T) \cdot V_M(\epsilon) \qquad (2)$$

From dilatometric measurements on Ti–50.4 at % Ni alloy it appeared that V_{HTP} increases exponentially with temperature within the range A_s–A_f. $V_{HTP}(T)$ could be expressed as:

$$V_{HTP}(T) = 1 - \exp \frac{-K(T-A_s)}{A_f - T} \qquad (3)$$

where K is a constant which by analogy to chemical reactions, can be considered as a reaction rate constant. It is to be noted that the type of Equation 3 has been found empirically to describe the kinetics of a wide variety of reactions in metals [11].

The probability that re-orientation of an existing martensite occurs under an external stress is expected to be proportional to the number N of martensite variants that are crystallographically equivalent. If, as has been assumed, all the variants exist with equal probability, the interfaces contained in the microstructure (twin boundaries in the case of Ni–Ti [7]) assume all the possible orientations with respect to the applied stress. Therefore some martensite variants would be un-affected and others would be affected to different extents depending on their relative orientation. It

then follows that V_M would never achieve unity for any finite strain. A relation which gives V_M as a function of ϵ must then satisfy the following conditions:

$V_M = 0$ for $\epsilon = 0$, and

V_M increases with ϵ (as measured from the zero-point) but never achieves unity.

These conditions can be satisfied by an exponential function of the form:

$$V_M = 1 - \exp(-C\epsilon) \qquad (4)$$

where C is a constant that can be taken to be the number N of crystallographically equivalent martensite variants.

$\sigma_r(T,\epsilon)$ can then be expressed as:

$$\sigma_r(T,\epsilon) = \sigma_Y^{HTP} \left\{ 1 - \exp \left[-K \left(\frac{T-A_s}{A_f - T} \right) \right] \right\}$$
$$\times [1 - \exp(-N\epsilon)] \qquad (5)$$

The characteristic features of the recovery stress as depicted from Equation 5 are:

(i) For a given strain ϵ, σ_r is sensitive to temperature only within the range A_s–A_f.

(ii) σ_r achieves its maximum value of:

$$\sigma_r(max) = \sigma_Y^{HTP}[1 - \exp(-N\epsilon)] \qquad (6)$$

at the A_f temperature where $V_{HTP} = 1$.

(iii) For temperatures higher than the A_f, σ_r becomes sensitive only to strain.

These features are in agreement with the experimental observations [5, 6]. Experimental work is now in progress in order to compare the measured and predicted values of the recovery stresses developed by a Ni–Ti alloy.

References
1. J. PERKINS, editor, "Shape Memory Effect in Alloys" (Plenum Press, New York, 1975).
2. R. BANKS, *Naturwissenschaften* **62** (1975) 305.
3. R. BANKS, "Shape Memory Effects in Alloys", edited by J. Perkins. (Plenum Press, New York, 1975) p. 537.

4. R. BANKS and M. WAHLIG, Presented at the International Solar Energy Society Meeting, Winnipeg, Canada (1976) Lawrence Berkeley Laboratory Report No. 5293.
5. G. R. EDWARDS, J. PERKINS and J. M. JOHNSON, *Scripta Met* 11 (1975) 1167.
6. W. B. CROSS, A. H. KARIGITS and F. J. STIMLER, "Nitinol Characterization Study," NASA Contractor Report (1969) Cr-1433.
7. H. A. MOHAMED and J. WASHBURN, *J. Mater. Sci* 12 (1977) 469.
8. *Idem, Met. Trans.* 7A (1976) 1042.
9. C. M. WAYMAN, "Shape Memory Effects in Alloys", edited by J. Perkins. (Plenum Press, New York, 1975) p.1.
10. L. DELAEY, R. V. KRISHNAN, H. TAS and H. WARLIMONT, *J. Mater. Sci.* 9 (1974) 1521.
11. J. BURKE, "The Kinetics of Phase Transformations in Metals" (Pergamon Press, Oxford, 1965) p. 45.

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On $Al_2 M$-type phases in splat cooled aluminium alloys

As part of a systematic investigation on the structure of rapidly solidified aluminium alloys, we have studied the structure and the decomposition behaviour of a rapidly solidified aluminium–2 at% platinum alloy. The present communication reports the observation of a non-equilibrium phase $Al_2 Pt$ in the as splat foils. Fig. 1a shows a typical microstructure and Fig. 1b gives the corresponding diffraction pattern. The diffraction pattern can be indexed in terms of a cubic cell with lattice parameter $a = 5.67 \pm 0.03$ Å. On heating, within the error of the electron diffraction, an increase in the lattice parameter was observed. One of the features of the diffraction pattern is the absence of the 200 reflection. Among the equilibrium phases in the alu-minium–platinum system, the only phase which has close similarity to the above structure is $Al_2 Pt$. This phase has the CaF_2 type of structure and its lattice parameter is reported to be 5.922 Å [1]. However, the structure exhibits a weak 200 reflection.

In a similar experiment with Al–8 wt% Fe, Stowell and co-workers [2] observed a cubic phase with lattice parameter 5.85 Å during the precipitation of iron from the single phase region of the splat foil. They assigned a diamond cubic structure to this phase, which accounts for the absence of the 200 reflection. However, the calculated atomic volume of the structure is 25.03 Å^3 which is very different from the atomic volumes of aluminium (16.60 Å^3) or iron (12.12 Å^3). By assigning the CaF_2 structure to $Al_2 Fe$ (metastable), the atomic volume (16.68 Å^3) turns out to be close to the atomic
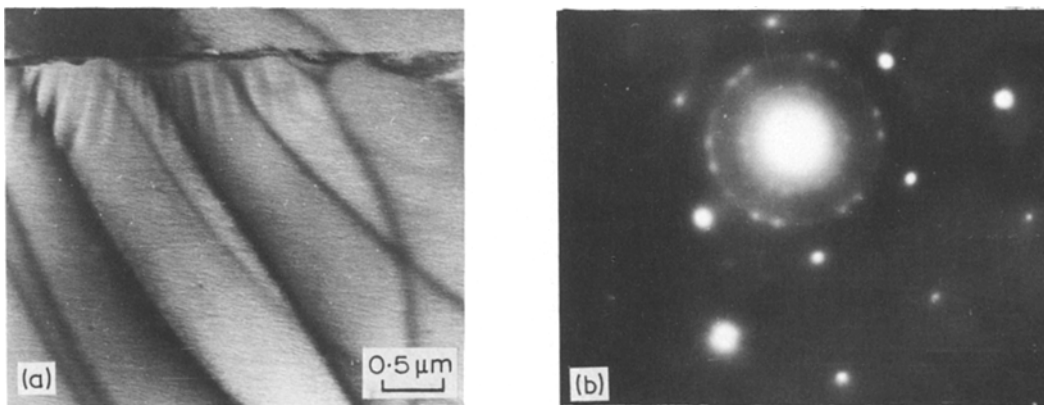

Figure 1 (a) As-quenched structure in Al–2 at% Pt alloy. (b) Electron diffraction pattern of the region shown in Fig. 1a.