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Thermal Expansion Studies of Pre-transformation Behaviour

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ABSTRACT

Many structural phase transformations in metals are characterised by anomalous pre-transformation behaviour in their physical properties. The development of pre-transformation distortion of the crystal lattice is a significant feature that has been widely studied by a variety of diffraction techniques. Although thermal expansion measurements provide a direct measure of bulk thermal strain with significantly more sensitivity than possible with diffraction studies, they have received limited application to pre-transformation studies. The A15 structure compound, V_3Si and the alloys In-Tl and Ni-Al have been studied in some detail in recent years. In the work under review here, the influence of stress, either externally applied or attributed to sample microstructure is observed to be a prominent factor in determining the pre-transformation behaviour.

INTRODUCTION

The term 'martensitic transformation', which originally referred to the structural change that occurs in a number of ferrous alloys, is now in common usage for a wide range of structural transformations that can be generally characterised as proceeding by diffusionless shear displacement. A feature of the martensitic transformation is the precursor effects that have been observed in a range of physical properties at temperatures well above the transformation temperature, T_M (Finlayson, 1983). The field of pre-transformation behaviour in relation to displacive transformations was the topic for a recent symposium (Pre-transformation Behaviour, 1986).

While diffraction studies provide the most comprehensive information on the structural and dynamic nature of the martensitic transformation, thermal expansion measurements can give a direct and very sensitive measure of bulk dimensional changes. However, use of the technique has been limited to V_3Si (Fawcett, 1971; Fukase et al., 1978; Milewits and Williamson, 1978; Gibbs et al., 1981; Ott et al., 1985), In-Tl solid solution alloys (Pahlman and Smith, 1968; Liu et al., 1990) and a Ni-Al alloy (Liu et al., 1991). It is the purpose of this paper to review these measurements.

EXPERIMENTAL DETAILS

The majority of the expansion measurements were made in capacitance dilatometers either identical or similar in design to that described by White and Collins (1972), with the remainder being made in an interferometric dilatometer (Pahlman and Smith, 1968) and by push-rod dilatometry (Liu et al., 1990, 1991). It is a feature of both the capacitance and push-rod dilatometers that the sample is subjected to a modest stress (typically $\sim 10^5$Pa), which, while complicating the interpretation of the data, does provide information on the influence of stress upon the transformation.

REVIEW OF THERMAL EXPANSION DATA

V_3Si

The martensitic transformation which occurs for the A15 structure superconductor, V_3Si, has been extensively studied by a wide range of experimental techniques (Weger and Goldberg, 1973; Testardi, 1973, 1977). Dramatic precursor behaviour is observed in the temperature dependence for the $c'(= \frac{1}{2}(c_{11} - c_{12}))$ elastic constant for V_3Si. This constant, which is associated with a $[110][1\bar{1}0]$ elastic wave, decreases towards zero on cooling from room temperature indicating the developing instability of the crystal for this particular shear wave. The martensitic transformation (which does not always occur) at around 22K involves a cubic to tetragonal distortion which Batterman and Barrett (1966) have shown is the result of a double $\{110\}\langle 1\bar{1}0\rangle$ shear on $\{110\}$ planes orientated at 60° to each other. In the case of V_3Si, $c/a > 1$.

In the absence of applied stress the orientation of the habit boundary separating the martensitic phase from the parent cubic phase will be determined by energy considerations due to the crystal imperfections with the formation of any of the possible six martensite variants. However, the application of an external stress pre-disposes the crystal to transform so that an a axis is parallel to the direction of the stress. This is illustrated in Figure 1 taken from Patel and Batterman (1966).

There have been several independent investigations of the thermal expansion of V_3Si, both for single crystals (Fawcett, 1971; Fukase et al., 1978; Milewits and Williamson, 1978; Ott et al., 1985) and polycrystalline material (Patel and Batterman, 1966; Gibbs et al., 1981). The influence on the expansion of the stress applied to the sample during the measurements is striking. This is illustrated in Figure 2, reproduced from the report by Fukase et al. (1978). The only difference between the two sets of data is the distribution of the load (200 g.wt) applied to the sample over the entire sample cross-section in method B as against the local loading in method A, yet the effect on the expansions measured along $[1\bar{1}0]$ and [110] is dramatic.

With the exception of the measurements of Ott et al. (1985), there is general consistency that the expansion coefficient along a cubic axis is large and positive, i.e. exhibits tetragonal phase, a-axis behaviour as the transformation temperature is approached. In the case of Ott et al., their measurements along the [100] are more consistent with a precursor c-axis-type expansion. (See Figure 3.)

Ott et al. (1985) ascribe the difference in the expansion measurements to the influence of the applied stress on the transformation. Thus, whilst a-axis behaviour was preferred for previous measurements along a cubic <100> axis on account of the small applied stress, in their measurements the applied stress was presumed to be too small to predetermine the transformation structure.

A striking illustration of the influence of stress upon the pre-transformation expansion behaviour is seen for polycrystalline material. When Smith et al. (1975) first reported a large, negative expansion coefficient for polycrystalline V-Si compounds, it was assumed that this behaviour was a feature of the cubic phase and a manifestation of the anharmonicity. Subsequent measurements (Gibbs et al., 1981) for V 25.75 at% Si revealed a highly anisotropic expansion behaviour (Figure 4) extending up to temperatures as high as 90K and, therefore, well above the transformation temperature.

Optical microscopy on the polished faces of the three prisms that had been cut from the argon-arc-cast ingot revealed a strongly preferred orientation in the grain structure, with columnar-like growth originating from the side of the ingot which was in contact with the water-cooled hearth (Figure 5). Thus, the a-axis-like results taken in the orientation perpendicular to both the ingot axis and the plane of the hearth (the open circles in Figure 4) predominantly represent the expansion along the long axis of the grains. It then follows that there is predominantly c-axis behaviour along the axis of the ingot (perpendicular to the direction of grain growth) and mixed a- and c-axis behaviour in the remaining direction.

Unsuccessful attempts to grow single-crystal V_3Si by zone melting (Gibbs, 1983) resulted in a V 25.5 at% Si ingot with columnar grain growth along its axis. The expansion data taken along the axis and in two mutually orthogonal directions perpendicular to the axis are shown in Figure 6. Here the anisotropy

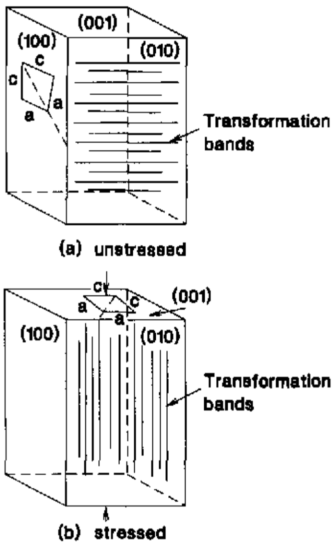

Fig. 1 Transformation bands in unstressed and stressed V_3Si (Patel and Batteman, 1966).

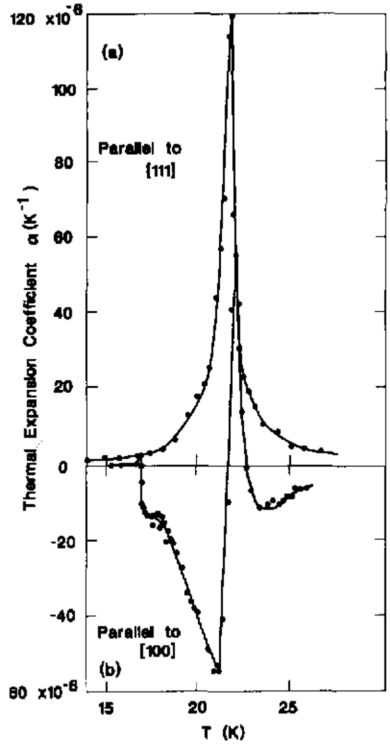

Fig. 3 [111] and [100] expansion coefficient for V_3Si (Ott et al., 1985)

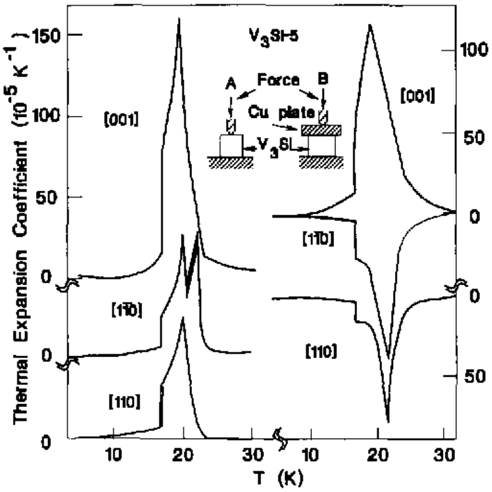

Fig. 2 Expansion coefficient for V_3Si along [001], [1$\bar{1}$0], [110] under different conditions of applied stress (Fukase et al., 1978)

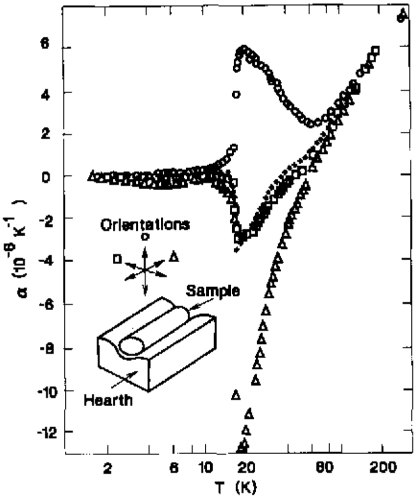

Fig. 4 Linear thermal expansion for V 25.75 at% Si along three mutually orthogonal axes as indicated in insert (Gibbs et al., 1981)

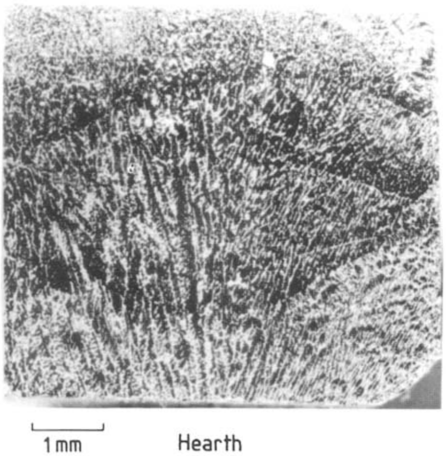

Fig. 5 Optical micrograph for V 25.75 at% Si expansion specimen showing a section orthogonal to both the hearth and the axis of the ingot.

exists up to about 60K, with the c-axis behaviour occurring parallel to the grain-growth direction. From these observations it is concluded that the direction of grain growth is not the factor in determining the crystal morphology at the transformation.

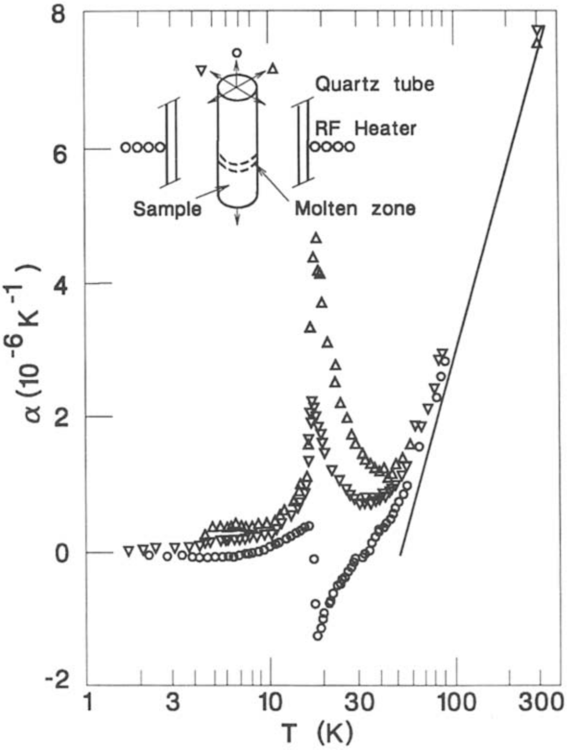

Fig. 6 Linear thermal expansion for polycrystalline V 25.5 at% Si measured along three mutually orthogonal axes as indicated in insert. (Gibbs, 1983)

The configuration of the residual-stress field in the ingot will be determined by the thermal gradients established during cooling from the melt. In both cases the thermal gradient is perpendicular to the axis of the ingot. However, whereas the zone-melted V 25.5 at% Si ingot would have experienced uniform cooling and hence the strain field is expected to have axial symmetry, the arc-cast V 25.75 at% Si ingot cooled by contact with the hearth and consequently is expected to have a highly anisotropic strain field. Thus, the V 25.5 at% Si exhibits axial symmetry in its a-axis expansion behaviour, whereas the V 25.75 at% Si only has predominantly a-axis character in the direction perpendicular to both the ingot axis and the hearth.

Indium-Thallium Alloys

Indium and thallium form a continuous series of disordered solid-solution alloys in the composition range 15.5 to 31 at% Tl which undergo a martensitic transformation on cooling, with the structural transformation temperature, T_M, ranging from 425K to near 0K, respectively (Pollack and King, 1968). The face-centred cubic to face-centred tetragonal transformation is preceded by a softening of the c′ elastic constant and involves the same double $\{110\}<1\bar{1}0>$ shear described for the A15 structure transformation.

The first detailed thermal expansion study of the transformation was made by Pahlman and Smith (1968) with measurements on a series of single-crystal samples along a [110] direction in the cubic phase. These measurements were made in an interferometric dilatometer in which the changes in the sample length were transmitted to the interferometer by a quartz push-rod. Thus these measurements, which were only made in a single [110] direction for each sample, were obtained with the sample subjected to an unknown stress applied in the direction of measurement. In addition to the large anomaly observed at T_M for the In 26.57 at% Tl and In 27.88 at% Tl alloys, a broad minimum in the expansion coefficient was found in the cubic phase centred around 220K. A maximum in the expansion behaviour at low temperatures was also reported for two alloys (In 31.16 and 34.28 at% Tl) that remained cubic over the temperature range of the measurements.

Anomalous structural behaviour for an In 25 at% Tl single crystal has also been observed in the cubic phase about 100K above T_M, using neutron scattering (Wilkins et al., 1982).

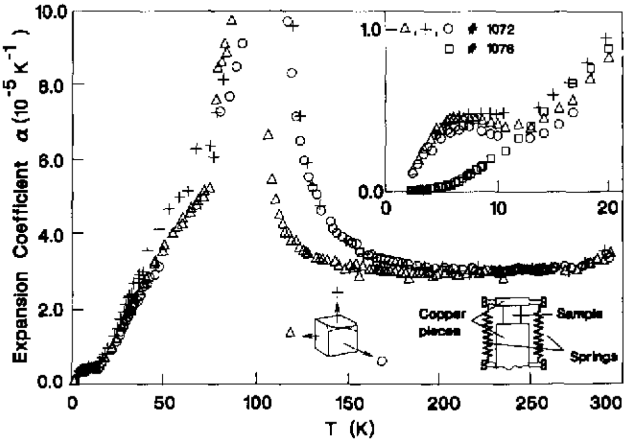

Fig. 7 Thermal expansion for an In 26.5 at% Tl single crystal along the three <100> axes. The sketch at bottom right shows the sample mounting. The insert shows the low temperature expansion (Lui et al., 1990).

Measurements of the thermal expansion along the three <100> axes of the cubic phase of a transforming In 26.5 at% Tl single crystal have been reported (Liu et al., 1990) together with a [100] measurement for a non-transforming In 35.7 at% Tl single crystal. The expansion coefficients for the three directions in In 26.5 at% Tl are reproduced in Figure 7 where the data above 50K were taken as the sample was cooled. T_M, defined as the mid-point of the abrupt change in the sample length, varied from 105 to 116K for the three sets of data. On a heating run, T_M was approximately 13K higher.

Although there are some differences in the values for the expansion coefficient, the measurements in the three <100> directions do not show any significant anisotropy above or below T_M. An anomalous temperature dependence is seen below 15K, but the expansion coefficient is still essentially identical in all three directions. It was pointed out that this expansion behaviour both in the vicinity of T_M and at low temperatures is consistent with the direction of measurement always being a tetragonal phase a-axis. In the case of the low-temperature behaviour, the argument is based upon a similarity with the a-axis expansion for indium (Collins et al., 1967).

Thus, again the application of an external stress is apparently pre-determining the direction of the tetragonal-phase a axis. Data taken in a push-rod dilatometer indicated that a stress as small as 2×10^4Pa (the lowest that could be applied) was sufficient to pre-determine the a axis.

No evidence was seen for the "high temperature" anomalous expansion behaviour reported by Pahlman and Smith (1968) or for the "structural" anomaly observed in the cubic phase by Wilkins et al. (1982). However, it is clear that the pre-transformation contribution to the expansion extends to temperatures well above T_M.

Nickel-Aluminium Alloys

Ni_xAl_{1-x} alloys in the composition range $0.615 < x < 0.64$ transform martensitically from a CsCl-type structure by shears of the $\{110\}<1\bar{1}0>$ type to a 7M-(5,-2) stacking (Noda et al., 1990). Precursor softening of the transverse $\{110\}<1\bar{1}0>$ phonon mode is again associated with the transformation (Shapiro et al., 1986). The onset temperature, M_s, as determined from optical observations of the onset of surface relief (Au and Wayman, 1972; Chakravorty and Wayman, 1976), varies between 0 and 400K as x increases.

A thermal expansion study of the transition has been made (Liu et al., 1991) for a Ni 37.5 at% Al single crystal that had been previously studied by neutron scattering (Shapiro' et al., 1986, 1989). The latter work gave $T_M \sim 80$K. Measurements, which were taken along the three <100> cubic phase axes, in a capacitance dilatometer, are reproduced in Figure 8. As there are rapid fluctuations in thermal strain in the temperature range 130-200K, that are attributed to surface tilting, the data are displayed as thermal strain as a function of temperature instead of the conventional expansion coefficient.

As can be seen from Figure 8 the (negative) strain increases isotropically as the crystal is cooled from room temperature to 200K. The anomalous fluctuations referred to above are then observed for two of the measuring directions (denoted as A and C) but not for the third, B direction. This behaviour can be seen in the insert to Figure 8. In spite of the apparent irregularity of the changes in thermal strain (which were examined in more detail in a push-rod dilatometer) the temperatures at which they occur were reproducible.

An optical examination of the sample surfaces established that surface tilts, resulting from the formation of martensite bands, were responsible for the fluctuations in thermal strain. Bands were observed on the faces perpendicular to the A and C directions, but not on the face perpendicular to the B direction. (See Figure 9.)

On cooling below 135K the anisotropy in the thermal strain develops rapidly with strong contraction in the A direction and equally strong expansion along the C direction. The strain for the B direction shows relatively little change. This distinct triaxial behaviour continues until an abrupt discontinuity occurs in all three sample dimensions at the martensitic transformation.

Liu et al. argue that this expansion behaviour is consistent with a pre-transformation development of an orthorhombic, pseudo-single crystal with its c axis (longest), a axis (shortest) and b axis along the C, A and B directions of measurement, respectively, arising from preferential orientation of the martensite variants. However, they note that the pseudo-single crystal behaviour does not hold through the transformation both for the sign and magnitude of strains on the a and c axes.

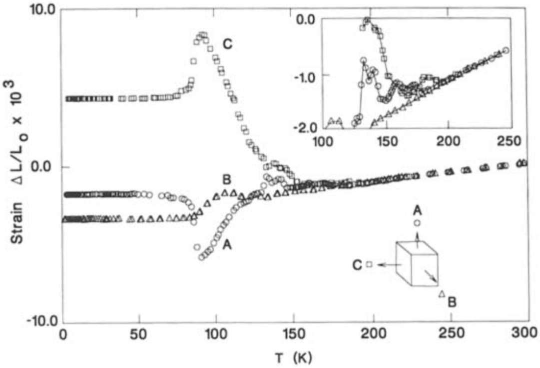

Fig. 8 Thermal strain for single crystal Ni 37.5 at% Al along the three <100> cubic axes. The insert shows the detail in the temperature range 100-250K. (Lui et al., 1991)

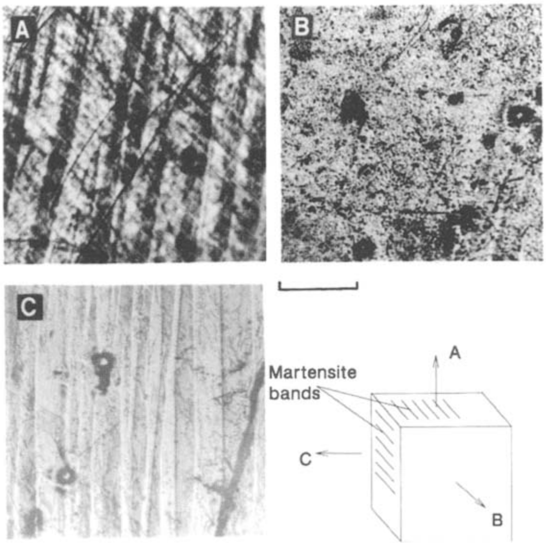

Fig. 9 Photomicrographs of sample surfaces normal to A, B and C axes. The horizontal bar, bottom-left corner, B, corresponds to 200μm.

The above interpretation of the pre-transformation expansion was supported by a study of its stress dependence in a push-rod dilatometer in which the stress applied to the sample could be varied between 2 and 28 × 10^4Pa. The application of stress increased the magnitude of the pre-transformation strain measured in the A direction, whereas it decreased it for the C direction. This is consistent with the favoured establishment of variants with the shortest (a) axis of the orthorhombic phase aligned along the direction of the applied stress.

While the applied stress influences the preferential orientation of variants, the impact for the Ni-Al alloy is significantly less than the effects of stresses for In-Tl or V_3Si. This may be understood from the fact that for both In-Tl and V_3Si there are only six possible martensite variants, whereas for Ni-Al there are twenty four (Noda et al., 1990). Thus, it is to be expected that the forced pre-selection of the orientation of variants along a specific direction by the application of stress should be easier for In-Tl and V_3Si than for Ni-Al.

CONCLUSIONS

Measurements of thermal expansion by dilatometry provides a sensitive means of studying pre-transformation behaviour. It is possible to detect both bulk and surface effects that occur well above the martensitic transformation. The technique also provides information on the influence of applied stress on the orientation of the pre-transformation martensite variants.

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