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Calorimetric and ultrasonic investigation of the R-phase formation in a TiNi:Fe alloy

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Abstract. We report a systematic calorimetric study of the formation of the R-phase in a polycrystalline TiNi:Fe alloy, conducted using a high-sensitivity scanning device. Thermograms performed at very slow heating/cooling rates always appear as an overlap of two peaks. The high-temperature peak does not present any hysteresis and is associated with a continuous transition to the intermediate incommensurate phase. Extrapolation at zero heating/cooling rates gives a value of 1.8 K for the intrinsic thermal hysteresis of the second peak at lower temperatures, ascribed to the first-order transition from the incommensurate to the R-phase. The paper also reports ultrasonic measurements on this alloy. Elastic anomalies in both longitudinal and shear elastic constants and in the ultrasonic attenuation have been detected in the same temperature region as the overall thermal effect.

1. Introduction

The equiatomic transition metal NiTi alloy undergoes a martensitic phase transition around room temperature. Preceding this transition, various premonitory effects have been reported. These effects occur at a temperature only slightly above the martensitic transition temperature (T_M) and have been ascribed to the transition from the CsCl ordered structure (B2-phase) to a rhombohedral phase (the so-called R-phase), via an intermediate incommensurate phase [1–3]. Much theoretical and experimental effort has been made to investigate these transformations [1, 4–6].

It has been shown [7] that the addition of a small amount of Fe (around 3%), which is substitutional for Ni, drops T_M towards much lower values, or even suppresses the martensitic transition, leaving the premartensitic effects almost unaltered. This observation indicates that the observed premartensitic effects are not premonitory of the martensitic transition, but are actually due to independent phase transitions. The addition of Fe, therefore, increases the temperature range to where the B2 to R-phase change can be studied without interference from the martensitic transition.

The transition to the R-phase results in anomalies in a number of physical properties of the system. Electron and x-ray diffraction experiments have evidenced the

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existence of diffuse scattering at $q_I = 1/3(111)$ and at $q_{II} = 1/3(110)$ within the premartensitic region [2]; also inelastic phonon scattering reveals phonon softening near the superlattice vector q_{II} associated with the TA_2 mode [8]. Ultrasonic measurements have been carried out in monocrystalline and polycrystalline NiTi alloys [9–12]. The values obtained for the elastic constants agree with the slopes at $q = 0$ of the phonon dispersion curves [13], and decrease of $C_L(=(C_{11}+C_{12}+2C_{44})/2)$, C_{44} and $C'(=(C_{11}-C_{12})/2)$ on reducing temperature has been observed. Other experimental techniques such as electrical resistivity, calorimetry and magnetic susceptibility measurements have also been used in order to characterize the formation of the R-phase [3, 14]. The results obtained by calorimetry and electrical resistivity are usually interpreted in terms of a single phase transition with first-order character; in particular, a few calorimetric measurements seem to indicate the existence of a transition latent heat [14]. On the other hand, diffraction experiments indicate the presence of an intermediate incommensurate phase at slightly higher temperatures than the R-phase. The transition from the B2 to the incommensurate phase is acknowledged to be continuous [13].

The aim of this work is to report: (i) systematic calorimetric measurements during cooling and heating through the R-phase using a high-sensitivity device and (ii) measurements of the temperature dependence of ultrasonic velocity and attenuation, in a polycrystalline NiTi:Fe alloy. These measurements have been complemented with measurements of magnetic susceptibility.

2. Experiment

An alloy with nominal composition $Ti_{50}Ni_{46.8}Fe_{3.2}$ was prepared from high-purity materials. Atomic absorption analysis showed that the composition conformed with the above formula. The material was annealed at 1170 K for 600 s in a controlled Ar atmosphere and was then quenched in water at room temperature.

From this rod we cut samples for calorimetric measurements and samples for ultrasonic experiments; the latter had two parallel faces (better than 10^{-3} rad), polished to give surface irregularities of about 2 μm. A small sample (108.9 mg) was also cut for magnetic susceptibility measurements. Differential scanning calorimetry measurements were conducted using a high-sensitivity microcalorimeter [15] (about 400 mV W^{-1} at room temperature) which employs two semiconducting thermoelectric power elements as heat flow transducers, mounted differentially on top of a massive copper block of large thermal inertia. The temperature of the copper block is monitored by a Pt-100 resistance thermometer. The temperature range of operation is from around 100 to 370 K.

The velocity and attenuation of ultrasonic waves was determined by a phase sensitive pulse-echo system [16] (MATEC, MBS-8000). Both X-cut and Y-cut transducers were used to generate and detect 5 and 10 MHz ultrasonic pulses. Acoustic coupling between sample and transducer was optimized using Dow Resin 276-V9 and Nonaq Stopcock grease in the temperature range 210 to 350 K and 77 to 270 K, respectively. The sample was placed on a copper plate the temperature of which was monitored by an embedded Pt-100 probe of a platinum resistance thermometer. Typical heating and cooling rates centre around 0.5 K min^{-1}. This is slow enough to ensure that both the sample and the copper plate are at the same temperature; nonetheless, a number of measurements were carried out by taking data at constant temperatures, which

ensured that ultrasonic time measurements did not depend upon the heating/cooling rate.

Magnetic susceptibility was measured during heating and cooling using a Faraday balance.

3. Results and discussion

Figure 1 shows the behaviour of the temperature derivative of the magnetic susceptibility, as a function of temperature. It is worth noting that the range of temperatures investigated (from 40 to 300 K) is much broader than previous measurements by Salamon *et al* [3]. On cooling, the derivative of the susceptibility shows remarkable peaks at around 240 and 90 K; on heating, peaks are located at around 170 and 245 K. The low-temperature peak is associated with the martensitic transition, which shows a remarkably large thermal hysteresis, and the high-temperature peak is ascribed to the formation of the R-phase and is consistent with the peak reported by Salamon *et al* [3].

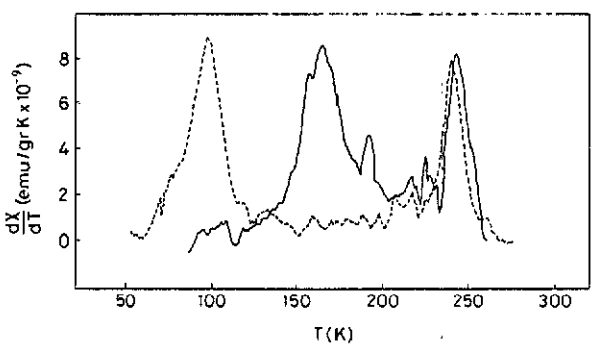

Figure 1. Temperature derivative of the magnetic susceptibility as a function of temperature for cooling (broken line) and heating (full line) cycles.

Electron diffraction experiments have also been carried out. The presence of extra spots associated with the incommensurate and R-phases has been observed at the expected temperature. Moreover, at around 90 K, a small amount of orthorhombic martensite has also been detected [17].

3.1. Calorimetric measurements

Typical thermograms are shown in figure 2. More than ten cycles have been performed for which an excellent reproducibility of the thermograms has been obtained. A calorimetric peak associated with the B2 $\rightleftharpoons$ R transition is detected at 241.0 ± 0.5 K on heating and 239.0 ± 0.5 K on cooling. Only a few calorimetric experiments in NiTi:Fe are reported in the literature. Salamon *et al* [3] measured the specific heat of $Ti_{50}Ni_{47}Fe_3$ using AC calorimetry; they reported a peak around 250 K with a thermal hysteresis, suggesting that the transition was first-order; no values for the enthalpy change were reported. On the other hand, Goo and Sinclair [14] reported a single differential scanning calorimetry (DSC) measurement during heating of a

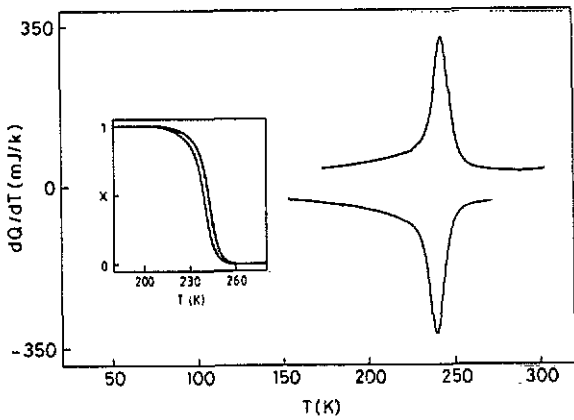

Figure 2. Typical thermograms of the B2 ⇆ R transition obtained during cooling (lower curve) and heating (upper curve). The inset shows the corresponding transformed fraction as a function of temperature.

$Ti_{50}Ni_{47}Fe_3$ alloy. A small peak was observed at around 260 K, from which these authors computed an enthalpy change of 3.75 J g^{-1}.

By numerical integration of the thermograms we have computed the effective enthalpy and entropy differences between B2 and R phases. Averaged values over four cycles, performed at heating/cooling rates between 1 and 2 K min^{-1}, are $\Delta H = -5.37 \pm 0.06$ J g^{-1}, $\Delta S = -0.0226 \pm 0.0005$ J g^{-1} K^{-1} for the B2 to R transition and $\Delta H = 5.35 \pm 0.07$ J g^{-1}, $\Delta S = 0.0222 \pm 0.0004$ J g^{-1} K^{-1} for the R to B2 transition. Values for the enthalpy change are higher than the value reported by Goo and Sinclair [14]; a possible source for this discrepancy could be the high performance of our calorimeter when compared to a classical DSC (see figure 2) together with an accurate determination of the base-line for integration [18].

Transformed fraction as a function of temperature can be computed from the calorimetric signal, as exemplified in the insert to figure 2; in the case reported, the specimen had a mass of 0.6990 g, the cooling/heating cycle was performed at a rate around 1.5 K min^{-1}, and the thermal hysteresis amounted to 3 K.

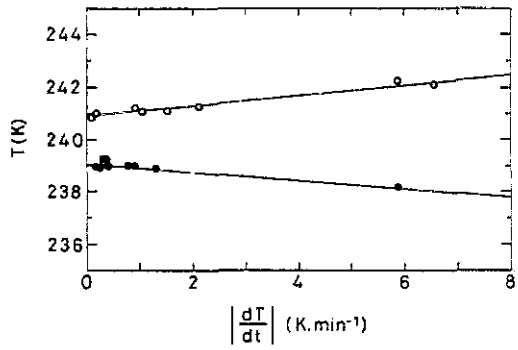

Figure 3. Peak temperature of the thermograms obtained in calorimetric cooling (●) and heating (○) cycles as a function of heating and cooling rate (in absolute value). The straight lines serve as guides to the eye.

In order to confirm that the observed thermal hysteresis is inherent to the tran-

sition and not purely due to the fact that the system is cooled and heated at finite cooling/heating rates, we performed a series of cycles at different heating and cooling rates using a sample of very small mass ($m = 0.074\,68$ g), so that thermal lag between specimen and calorimetric block is minimized. The temperature at which the resulting thermograms display a maximum is plotted in figure 3 as a function of cooling/heating rate. Extrapolation of these results to $\dot{T} = 0$ renders a value of 1.8 K for the intrinsic hysteresis. It is worth nothing that all the thermograms corresponding to calorimetric experiments carried out at very low heating/cooling rates systematically exhibit a double peak, as shown in figure 4; the high-temperature peak could be attributed to the transition to the incommensurate phase, which, as evidenced in the figure does not show any thermal hysteresis, while the low-temperature peak would be associated with the transition to the R-phase and shows the aforementioned hysteresis of 1.8 K. The fact that this is the case represents a calorimetric corroboration that the transition from the B2 to the R-phase takes place via an intermediate incommensurate phase, showing the expected continuous character of the transition to the incommensurate phase, and that the subsequent transition to the R-phase has a first-order character. Both transitions are separated by around 3 K.

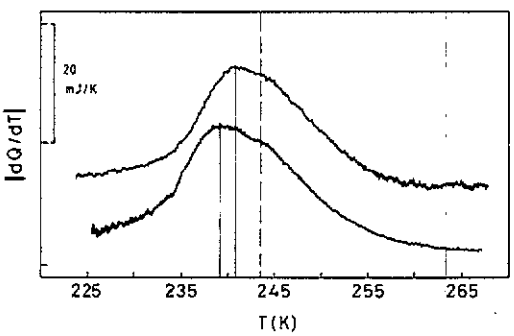

Figure 4. Thermograms corresponding to a very small specimen (mass of 0.074 68 g) and performed at a very low heating and cooling rate (0.11 and −0.29 K min^{-1} for the upper and lower curve, respectively). The broken vertical line indicates the location of a peak presumably associated with the transition between the B2 and the incommensurate phase. The continuous vertical lines indicate the location of the peaks corresponding to the transition between the incommensurate and the R-phase, which display a thermal hysteresis of about 1.8 K.

The peak in the derivative of the magnetic susceptibility is coincident with the calorimetric peak. The thermal hysteresis shown is comparable to the one displayed by calorimetric peaks allowing us to conclude that these magnetic anomalies, mainly due to changes in the density of states at the Fermi surface, are related to the formation of the R-phase. Nevertheless, due to the fact that a numerical derivative is needed, the results do not have the necessary accuracy to determine if there is any contribution to this anomaly from the continuous transition to the incommensurate phase.

3.2. Ultrasonic measurements

The polycrystalline nature of our sample has resulted in a marked attenuation of the ultrasonic waves due to the scattering caused by grains: for longitudinal waves only

two echoes were detected while for shear waves no echo was detected at room temperature. We have computed a velocity for longitudinal waves at 300 K of 5860 m s^{-1}. This value is around 10% larger than the value found by Pace and Saunders [9] for polycrystalline NiTi alloys in the B2-phase; the difference is probably due to the different grain size between the two samples.

In the R-phase, the ultrasonic attenuation is much lower and reasonable echoes have become detectable for both longitudinal and shear waves; this has enabled us to measure the velocity for both modes and to compute the effective elastic moduli of this phase. The values for the bulk modulus and the shear modulus at 130 K are 189 GPa and 30 GPa, respectively.

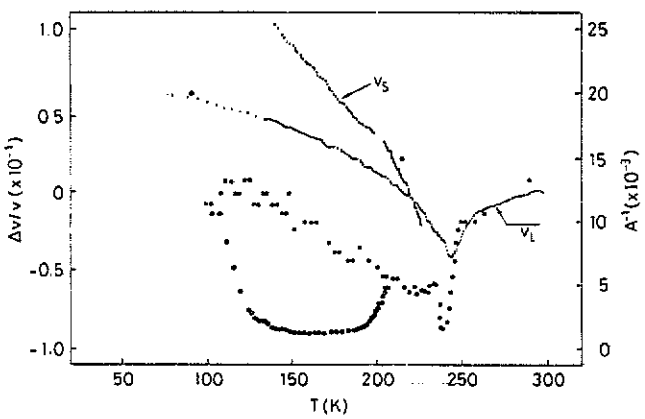

Figure 5. Relative change of the ultrasonic velocity (dotted lines) for longitudinal (v_L) and shear (v_S) waves, and inverse of the amplitude of the first ultrasonic echo as a function of temperature for longitudinal (●) and shear (○) waves.

The relative change of the ultrasonic velocity with temperature is plotted in figure 5, for both longitudinal v_L and shear v_S waves. A remarkable change in behaviour is observed when the sample transforms to the R-phase. In the B2-phase v_L decreases with reducing temperature while in the R-phase it regains the usual behaviour of increasing as the temperature drops. This reduction of v_L reflects a softening of the longitudinal elastic constant. Mercier *et al* [11] did not report noticeable changes of C_{44} and C' of Ti–Ni at the transition to the R-phase. A small anomaly was observed for C_{11}. While the present work was in progress, measurements in Ti–Ni single crystals in a broad temperature range were reported [12] which show anomalies for all the elastic constants at the transition temperature. The softening of the longitudinal elastic constant which we found for TiNi:Fe is consistent with the softening of C_L in Ti–Ni reported by Brill *et al* [12] which was mainly due to the softening of C_{44}.

It is worth mentioning that for stoichiometric Ti–Ni the martensitic transition takes place very close to the B2 $\rightleftarrows$ R transition; this makes it difficult to clearly ascribe the observed anomalies to one of the transitions; this is not the case for our TiNi:Fe sample in which both transitions are separated by more than 100 K. The fact that in the R-phase v_L increases with reducing temperature clearly indicates that the softening of the longitudinal elastic constant is related to the instability of the lattice associated with the formation of the R-phase and not to the martensitic transformation.

Shear waves could only be measured in the R-phase. v_S increases as temperature

is reduced indicating a stiffening of the shear elastic constant as predicted by the anharmonic theory. It is well established that materials undergoing martensitic transition exhibit a softening of C' [19]; therefore the increase of the averaged shear elastic constant found in our experiments indicates that C_{44} must increase as temperature is reduced. This again supports the fact that softening in C_{44} is only associated with the transition to the R-phase. A change in slope at 210 K is observed which could be due to a decrease of C' associated with the instability of the lattice towards the orthorhombic martensitic phase.

We also measured the ultrasonic attenuation of longitudinal and shear waves, as a function of temperature at 5 and 10 MHz. In the B2-phase, the attenuation for 5 MHz waves is lower than for 10 MHz but the behaviour with temperature is similar for both frequencies. In figure 5 we plot the inverse of the amplitude of the first ultrasonic echo as a function of temperature. Attenuation due to the polycrystalline nature of the sample is very important in the B2-phase, as previously mentioned. When the specimen undergoes a transition to the R-phase, the intragranular multidomain character of the R-phase [20] reduces the average size of the scattering objects, approaching the Rayleigh scattering regime [21]. This behaviour is parallel to the behaviour observed during the martensitic transition of Cu–Zn–Al alloys, for which a detailed study has recently been reported [22].

The drastic increase in the attenuation of shear waves observed at temperatures around 120 K is caused by the onset of the martensitic transition; this is confirmed by the magnetic susceptibility measurements (see figure 1).

4. Conclusions

We have investigated the change from the B2-phase to the R-phase in a polycrystalline TiNi:Fe alloy. Our systematic calorimetric study of the formation of the R-phase gives a plausible indication of the formation of an intermediate phase (the incommensurate phase) and has clearly demonstrated the first-order character of the transition to the R-phase. Integration of the whole calorimetric peak gives values for enthalpy and entropy changes in the transition of $\Delta H = 5.36 \pm 0.07$ J g^{-1} and $\Delta S = 0.0224 \pm 0.0005$ J g^{-1} K^{-1}. It is important to note that these values only represent an upper boundary since the contribution from the peak in C_p associated with the continuous transition to the incommensurate phase cannot be subtracted easily.

In addition, this work reports first measurements of ultrasonic velocity and attenuation as a function of temperature in a TiNi:Fe alloy around the B2 $\leftrightarrows$ R transition. Softening of the longitudinal elastic constant in the B2-phase is observed on approaching the transition, while in the R-phase both longitudinal and shear elastic constants stiffen on cooling, as expected from anharmonic lattice theories. Taking advantage of the fact that the B2 $\leftrightarrows$ R and the martensitic transitions are separated by more than 100 K in the alloy investigated, we have been able to show that softening of the longitudinal elastic constant is solely due to the B2 $\leftrightarrows$ R transition.

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