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# ac technique applied to $c_p$ measurements in Ni–Mn–Ga alloys

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## Abstract

The specific heats ($c_p$) of two single crystalline ferromagnetic shape memory alloys close to the stoichiometric $Ni_2MnGa$ have been measured by the ac technique in both quasi-isothermal and scanning modes. The measurements were carried out in a temperature range slightly broader than the transformation interval of each alloy. This allows getting reliable values of the $c_p$ difference between parent and martensite phases within the transformation range, which is important for the thermodynamic analysis of the thermoelastic martensitic transformation undergone by these alloys.

*Keywords:* Ni–Mn–Ga alloys; Magnetic shape memory alloys; Specific heat; ac calorimetry; Differential scanning calorimetry

## 1. Introduction

Ferromagnetic shape memory alloys (FSMA) have attracted much attention in the recent years, since the discovery of large magnetic-field-induced strains (MFIS) in alloys close to the stoichiometric $Ni_2MnGa$ [1]. Ni–Mn–Ga alloys have been, by far, the most studied FSMA, showing a broad range of thermoelastic martensitic transformation temperatures, $T_M$, the transformation taking place either in the paramagnetic state ($T_M > T_C$, $T_C$ being the Curie temperature for ferromagnetic ordering) or in the ferromagnetic phase ($T_M < T_C$), which is obviously the case of interest in order to get giant MFIS [2]. In addition, a rich variety of martensitic structures, as well as pre- and inter-martensitic transformations thermally or stress-induced are shown by Ni–Mn–Ga alloys [3–5].

In the thermodynamic analysis of martensitic transformations, in order to sort out the different contributions to the thermoelastic balance (usually called “chemical” and “non-chemical” terms, the latter including elastic energy stored as well as dissipative terms) it is necessary to know the specific heats ($c_p$) of the phases – parent and martensite – involved [6]. Normally it is assumed that their difference is negligible, although in most cases this assumption is not well justified, as the $c_p$ values of both phases are not know. To the author’s knowledge, there are no data on the $c_p$ of Ni–Mn–Ga alloys, allowing for comparing directly the specific heats of parent and martensite phases in a temperature domain that includes the transformation range. Only $c_p$ values, in parent phase, have been determined for a stochiometric $Ni_2MnGa$ in order to detect premartensitic effects at temperatures about 50 K higher than $T_M$ [7].

In this work we present the $c_p$ values for two single crystalline Ni–Mn–Ga alloys which undergo a thermoelastic martensitic transformation from the ferromagnetic parent phase; the transformation range, close to room temperature, represents the case of major interest in view of applying the MFIS. The $c_p$ values have been obtained by means of ac calorimetry, the measurements were performed both in parent and in martensitic phase at temperatures close to transformation range, as well as during the transformation itself. Runs at very low scanning rates (dynamical method) or in quasi-isothermal mode have been carried out; the latter allows to

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get proper $c_p$ values within the transformation temperature range, where the latent heat of transformation can easily disturb the ac measurements.

## 2. Experimental

An ac calorimeter developed by the authors has been used [8,9]. In this device the sample is placed on a heating resistance made of constantan wire. On the free side (top) of the sample a thermistor (Fenwall196-204 QAG-001), with negligible heat capacity compared to that of the sample, is used to detect its temperature variations. The set formed by the heater, the sample and the thermistor is placed in a copper block allowing for a proper temperature programming.

The heat capacity of the sample C is determined by measuring the temperature oscillations amplitude, $\Delta T_{\mathrm{ac}}$, through the following expression:

$$\frac{1}{\Delta T_{\mathrm{ac}}^2} = \frac{\omega^2}{Q_{\mathrm{ac}}^2} C^2 + \frac{P^2}{Q_{\mathrm{ac}}^2}$$

where $\omega$ is the power signal frequency, $Q_{\mathrm{ac}}$ the input power to the sample, and $P$ is accounting for the thermal losses. Both $Q_{\mathrm{ac}}$ and $P$ have to be determined through a proper calibration.

The input power signal is generated by a Hewlett-Packard 8116A function generator (minimum frequency 1 mHz, 0.01 mHz resolution). The temperature variations in the sample are detected every 1.5 s with a Solartron 7061 multimeter (1 Ω resolution equivalent to 0.1 mK mean resolution in the scanned temperature range). More details of the ac calorimeter design and data treatment have been published elsewhere [8,9]. The ac system has been calibrated in the range 260–360 K using different Ni (99.99% purity) orthorhombic samples with 5 mm × 5 mm base and masses from 150 to 350 mg, according to the shape and weight of the Ni–Mn–Ga samples to be measured. The methodology followed in the calibration procedure has been exhaustively described in a previous work [8].

The quasi-isothermal measurements have been carried out by applying alternating power signals (30–50 mHz) to the sample, resulting in temperature oscillations with amplitudes between 4 and 8 mK. For the dynamical method, the power signal frequency was fixed at 40 mHz. A scanning rate of 0.56 mK/s (2 K/h) allows to obtain a $c_p$ value every 10 mK.

The $c_p$ was determined for two Ni–Mn–Ga single crystalline samples, from crystals grown by modified Bridgman method. Nearly orthorhombic samples with masses in the range 170–190 mg, with the following compositions and characteristics were used: Alloy N3: 49.4Ni–27.7Mn–22.9Ga (at.%); $T_{\mathrm{M}} = 275$ K ($T_{\mathrm{M}}$ is taken as the peak temperature on cooling in a typical DSC run) and $T_{\mathrm{C}} = 383$ K. Alloy G31: 52.0Ni–24.4Mn–23.6Ga (at.%); $T_{\mathrm{M}} = 323$ K and $T_{\mathrm{C}} = 360$ K.

Both alloys transform on cooling from the parent bcc $\mathrm{L2_1}$ ordered phase to a monoclinic martensite with modulations of five layers (10 M) [4], which is one of the typical martensites showing the MFIS.

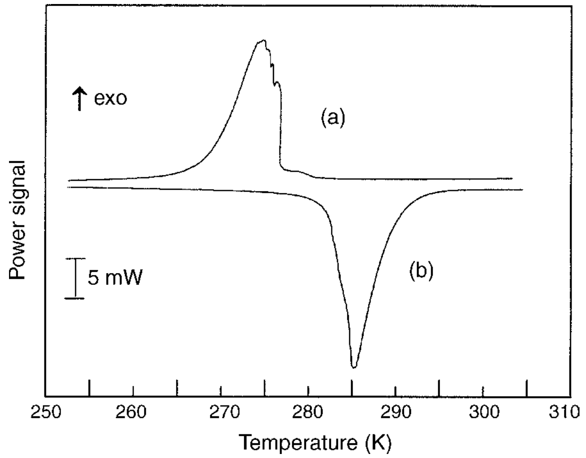

Fig. 1. DSC thermograms obtained for the sample N3 in the forward (a), and reverse (b) martensitic transformation.

## 3. Results and discussion

After the calibration procedure with pure Ni, several runs in dynamical mode as well as isothermal measurements were performed in a temperature span including the transformation range for both Ni–Mn–Ga samples. For the N3 alloy, the characteristic transformation temperatures are: $M_{\mathrm{s}} = 280$ K, $M_{\mathrm{f}} = 266$ K, $A_{\mathrm{s}} = 277$ K, $A_{\mathrm{f}} = 295$ K, where $M_{\mathrm{s}}$ and $M_{\mathrm{f}}$ stand for the start and finish of the direct, parent to martensite, transformation and $A_{\mathrm{s}}$ and $A_{\mathrm{f}}$ have the corresponding meaning for the reverse transformation. An example of a thermogram for the N3 alloy obtained in a DSC TA-2920 at 10 K/min is shown in Fig. 1.

Accordingly, ac runs were carried out in the range 260–295 K. Fig. 2 shows the $c_p$ values for the sample N3

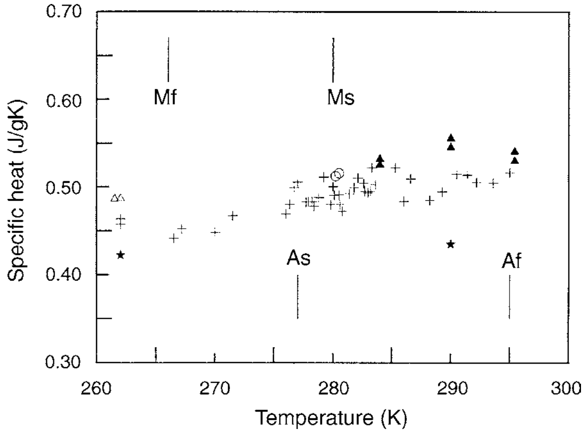

Fig. 2. Specific heat values for sample N3. Dynamic measurements +, quasi-isotherm measurements (parent phase (▲), martensite phase (△), and two-phase domain (◯)). The quasi-isotherm, two-phase data were obtained by stopping a heating run, thus at temperatures slightly above $A_{\mathrm{s}}$. The symbols (⋆) correspond to $c_p$ values for pure Ni.

obtained from the above mentioned experiments, i.e. dynamical runs on cooling and heating and quasi-isothermal measurements. As the main interest was to know the $c_p$ differences between both phases in the transformation range, the measurements were carried out from about 5 K below $M_f$ to about 5 K above $A_f$. The temperature dependence of $c_p$ either in martensite or in parent phase in these domains is below the resolution of our experimental set-up, and can be considered negligible. The same applies to the domain $M_f$–$A_s$ where the samples, once the direct transformation has been completed, continue to be fully martensitic on heating up to $A_s$; a parallel situation takes place on cooling from $A_f$ to $M_s$ for the parent phase. However, the specific heat for the martensitic phase $c_p$ (m) is slightly lower than that of austenite $c_p$ (p), both being not far from the pure Ni values (0.422 and 0.435 J/gK at 262 and 290 K [10], respectively; see Fig. 2). Further discussion of the results is carried out below.

Fig. 3 shows the thermograms for the direct and reverse martensitic transformation of the sample G31, obtained in the same experimental conditions as for the sample N3.

Considering the transformation temperatures for the G31 alloy, namely $M_s = 343$ K, $M_f = 313$ K, $A_s = 317$ K and $A_f = 347$ K, the corresponding ac runs were performed in the interval 310 K–352 K. The results are shown in Fig. 4. It is worth to note similar trends as for the sample N3, that is slightly lower $c_p$ (m) than for the parent phase, and a bit higher values for the alloy than for pure Ni.

It has to be pointed out that the $c_p$ values at temperatures within the transformation range, obtained by dynamical runs, can be affected by the heat exchange produced by the transformation/retransformation of small amounts of material even though the temperature amplitudes are very small. Examples of these "dynamical" values are shown in Figs. 2 and 4 to illustrate the scatter produced by the just mentioned effect. Depending of the transformation heat value, the jerkyness of the transformation and its hysteresis, the scatter in the specific heat within the transformation range can be more pronounced; an example in Cu-based alloys has been shown in Ref. [11]. At intermediate stages of the $p \leftrightarrow m$ transformation, only the $c_p$ values obtained under conditions as close as possible to isothermal ones can be considered as approaching properly the corresponding equilibrium values. It is worth to note that due to the transformation hysteresis, quasi-isothermal measurements of $c_p$ (m) can be obtained at temperatures $T$, such that $M_f < T < A_s$, by stopping the heating run of fully martensitic samples, and $c_p$ (p) values in an equivalent situation at $M_s < T < A_f$ stopping cooling runs of parent phase samples. $c_p$ values from quasi-isothermal measurements in these temperature domains are also shown in Figs. 2 and 4. For the quasi-isothermal measurements carried out, the temperature oscillations are much smaller than the thermal hysteresis of the transformation in the studied Ni–Mn–Ga alloys, therefore more reliable values for the $c_p$ than in dynamic mode can be obtained.

Taking into account the above considerations, from the measurements at temperatures out of the transformation domain, including the domains $M_f$–$A_s$ ($A_f$–$M_s$) on heating (cooling) for samples in fully martensitic (parent) phase, it is possible to establish the mean values of the specific heat in both phases: For the alloy G31, $c_p$ (m) = 0.50 J/gK at $T \approx 310\ \mathrm{K} < M_f$, and $c_p$ (p) = 0.55 J/gK at $T \approx 348\ \mathrm{K} > A_f$. For the alloy N3 the values are: $c_p$ (m) = 0.48 J/gK at $T \approx 263\ \mathrm{K} < M_f$, and $c_p$ (p) = 0.53 J/gK at $T \approx 297\ \mathrm{K} > A_f$. In both cases the estimated uncertainties are $\sim\pm 0.01$ J/gK, which correspond to the scatter within the isothermal values measured at the same temperature. The reproducibility is improved if the sample is not taken out of the calorimeter. Therefore, without the sample replacement uncertainty, it can be estimated that the $c_p$ difference between both phases is $\Delta c_p = 0.05$ J/gK, being the uncertainty of this difference not much larger than ±0.01 J/gK, in the temperature interval given by $A_f$–$M_f$. The $\Delta c_p$ value allows to calculate the

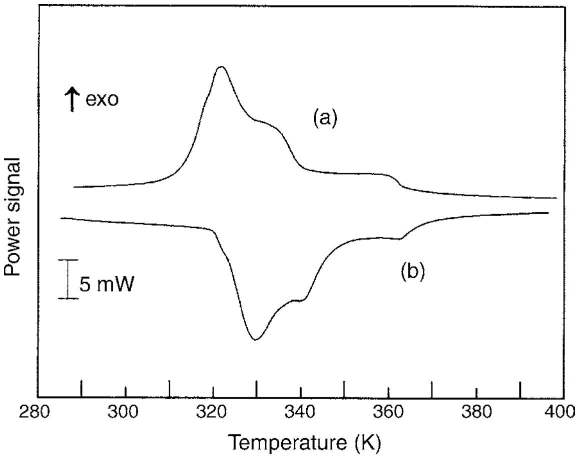

Fig. 3. DSC thermograms obtained for the sample G31 in the forward (a), and reverse (b) martensitic transformation. The Curie point can be seen as the kink in the calorimetric signal at ∼360 K.

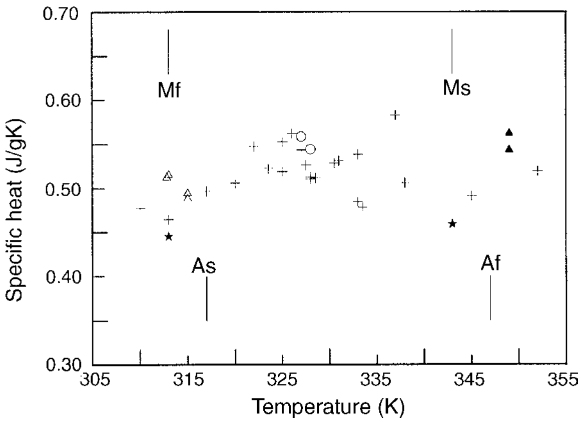

Fig. 4. Specific heat values for sample G31. Dynamic measurements +, quasi-isotherm measurements (parent phase (▲), martensite phase (△), and two-phase domain (○)). The quasi-isotherm, two-phase data were obtained by stopping a cooling run, thus at temperatures close the center of the $M_s$–$M_f$ interval. The symbols (⋆) correspond to $c_p$ values for pure Ni.

chemical enthalpy, entropy and chemical free energy differences for the transformation parent ↔ martensite at temperatures different from the equilibrium temperature $T_0$ for the m ↔ p transformation [6]. Assuming that $\Delta c_p$ does not depend on the temperature in the usual temperature interval of interest around $T_0$, i.e. $T_0 - T \leq 10$ K, as an example the correction for the enthalpy change at $T \neq T_0$ is simply $\Delta c_p$ $(\mathrm{T_0} - \mathrm{T})$. Thus, for an enthalpy change of 6.5 J/g, as for the alloy G31, the correction for $(T_0 - T) = 10$ K amounts 0.5 J/g, which can be significant in many thermodynamic estimations.

## 4. Conclusion

The ac device used in this work allows to obtain $c_p$ values with better accuracy than that offered by modulated DSC systems commercially available. For the alloy 52.0Ni–24.4Mn–23.6Ga (at.%, alloy G31) the $c_p$ values in parent and martensite phase, at temperatures close to the end of the reverse transformation ($A_\mathrm{f}$) or that of direct transformation ($M_\mathrm{f}$), respectively, are: $c_p$ (p) = 0.55 J/gK, $c_p$ (m) = 0.50 J/gK; For the alloy 49.4Ni–27.7Mn–22.9Ga (at.%, alloy N3), at the corresponding temperatures as before, $c_p$ (p) = 0.53 J/gK, $c_p$ (m) = 0.48 J/gK. The uncertainties are estimated to be close to ±0.01 J/gK in all cases. Eliminating the dispersion of results due to the sample replacement, the $c_p$ difference between parent and martensite is 0.05 J/gK for both alloys within the respective transformation range, with an estimated uncertainty slightly above ±0.01 J/gK.

In Ni–Mn–Ga alloys, the correction in the thermodynamic magnitudes of the martensitic transformation (i.e. enthalpy and/or entropy change) due to $c_p$ difference between the phases involved can be higher than 5% for typical values of the transformation heat and shifts in the equilibrium temperature $T_0$.

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