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Positron annihilation spectroscopy study of Ni-Mn-Ga ferromagnetic shape memory alloys

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Abstract

We have studied the role that vacancy type defects play in the martensitic transformation of Ni-Mn-Ga ferromagnetic shape memory alloys by means of positron lifetime spectroscopy. The measurements presented in this work have been performed in five ternary alloys. Three of them transform to modulated and two to non-modulated martensitic phases. With these five samples we cover a large range in composition. Positron experiments have been performed at room temperature after subsequent isochronal annealing at different temperatures and up to a maximum temperature of 600ºC. Results show a large variation of the average positron lifetime value with the isochronal annealing temperature in non-modulated samples. However, the response in the modulated samples is quite different. The results are discussed in term of different type of positron trapping defects and their evolution with the annealing temperature. The present work shows a correlation between vacancy concentration and martensitic transformation temperature of ferromagnetic shape memory alloys.

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Introduction

Since giant magnetic-field-induced strain (MFIS) was first reported on Ni-Mn-Ga ferromagnetic shape memory alloys (FSMA) by Ullakko et al. [1], a great amount of work has been performed to understand and improve the system in order to be implemented in practical devices [2-3]. The main drawbacks are the high brittleness, the low values of the martensitic transformation (MT) and the Curie temperatures of Ni-Mn-Ga alloys. These limitations have stimulated the research of new ferromagnetic shape memory alloys having better mechanical properties. Indeed, several studies have been performed to improve the mechanical and thermal properties [4-6].

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Different techniques have been used to analyze diverse properties of Ni-Mn-Ga alloys; however, very little work has been performed to study the role of vacancies in the martensitic transformation [7]. Positron annihilation spectroscopy is a very powerful technique to investigate vacancy-type defects in metals [8]. We have used positron annihilation spectroscopy measurements to study the role of vacancy-type defects in the modulated and non-modulated martensitic transformations of Ni-Mn-Ga polycrystalline alloys. Positron lifetime experiments have been performed at room temperature after subsequent isochronal annealing up to 600°C.

1. Experimental and computational method

Polycrystalline ingots of Ni$_2$MnGa were prepared from high purity elements by arc melting under protective Ar atmosphere. The ingots were homogenized in vacuum quartz ampoules at 1000 ºC during 24 hours. Small samples for calorimetric measurements were obtained from discs previously cut from the center of the ingots by slow speed diamond saw. These discs were used for positron lifetime measurements. Subsequent annealing treatments of 30 minutes at 900 ºC followed by quenching into ice water were performed on the alloys in a vertical furnace. Differential scanning calorimetry (DSC) measurements were carried out in a TA Q100 DSC instrument to study the thermal behavior of the alloys. The samples were polished after quenching in order to ensure a good thermal contact with the equipment. The MT temperatures of the as-quenched samples were obtained from DSC measurements performed up to 400 ºC at a heating/cooling rate of 10K/min. All DSC measurements were performed under nitrogen atmosphere.

For positron lifetime measurements a fast system with a resolution of 240 ps was used and a conventional $^{22}$Na source on a kapton foil was employed as the positron source. All lifetime spectra were analyzed after subtracting a constant source contribution. The statistic of each spectrum was always better than 1.6 millions of counts. For the isochronal annealing in positron annihilation measurements, the same heating/cooling rate of 10 K/min was used. The points in each positron lifetime curve correspond to the average obtained after 6-10 measurements. For all of the results the error is within the size of the symbols in the figures.

A study of five samples was conducted; three samples correspond to a modulated 7M (Pnnm space group) martensitic structure and two to a non-modulated structure (I4/mmm space group). The composition of the five samples can be seen in Table 1.

The theoretical calculations were performed first by solving self-consistently the electron density of the perfect or defected solid, using the tight binding version of the linear muffin-tin orbital method within the atomic-spheres approximation (LMTO-ASA). Second, calculations of the positron wave function were taken, and finally, the positron annihilation rate (the inverse of the positron lifetime) was obtained from the overlap of positron and electron densities as:

$$\lambda = \pi r_0^2 c \int dr \ n_p(r) \ n_e(r) \ \gamma(r)$$

where $r_0$ is the classical electron radius, $c$ is the speed of light in vacuum, $n_p(r)$ is the positron density and $\gamma(r)$ is the so-called enhancement factor, which has been taken into account using the generalized gradient approximation. For details about the computational method, see reference [9].

The positron lifetime calculations in the cubic structure of Ni$_2$MnGa, with lattice parameter of 0.58067 nm [10] have been performed in a supercell of 16 atoms (8 atoms of Ni, 4 atoms of Mn and 4 atoms of Ga).

|               | NM1  | NM2  | M1   | M2   | M3   |
|---------------|------|------|------|------|------|
| Ni            | 52.6 | 50.5 | 49.5 | 50.4 | 53.0 |
| Mn            | 26.7 | 30.4 | 28.5 | 25.2 | 21.0 |
| Ga            | 20.7 | 19.1 | 22.0 | 24.4 | 26.0 |

2. Results and discussion

2.1. Calorimeter measurements

Figure 1 shows DSC measurements carried out up to 400 ºC on the M1 sample quenched from 900 ºC. An endothermic peak at 20 ºC can be observed corresponding to the reverse MT (martensite-austenite). The change in
the baseline at around 80 ºC corresponds to the Curie temperature. It is also worth noting the presence of an exothermic peak at temperatures far above the MT temperature. This peak could be related to processes affecting the MT temperature [11]. The exothermic peak is observed only on the first heating up to 400 ºC, and it does not appear on subsequent cooling and posterior cycling of the alloy, so the peak must be linked to an irreversible process. After that cycling, a change in the MT temperature is observed. If consecutive thermal cycles from 150 ºC to 400 ºC inside the exothermic peak temperature range are done a growth in MT temperature is observed. The calorimetric measurements show a change in the MT temperature during the isochronal annealing process. This can be understood like an ordering process [11].

![Figure 1. DSC measurement performed in M1 sample.](image1)

![Figure 2. DSC measurements showing the exothermic peaks for samples NM1 and NM2.](image2)

Figure 2 shows the exothermic peaks of NM1 and NM2 samples. In the case of the non-modulated NM1 and NM2 samples the presence of small endothermic peaks at temperatures above 200 ºC indicates that the reverse MT has not been fulfilled at this temperature. This indicates a defect pinning of the martensite-austenite interfaces, which may be a consequence of the high concentration of defects in the martensite phase due to the quenched-in process [12].

The exothermic peak of NM2 sample is shifted to higher temperature around 50 ºC with respect to the peak corresponding to NM1 sample, see figure 2. This indicates that the ordering processes occur in NM2 sample at higher temperature than in NM1 one.

2.2 Positron lifetime measurements in non-modulated samples

Figure 3 shows the behavior of the average positron lifetime ($\tau_{av}$) as a function of isochronal annealing temperature for NM1 sample. The curve has been divided in four regions, denoted by “region 0”, “region I”, “region II” and “region III”. The first values of the average positron lifetime on the curve of figure 3 amounts to 185 ps and corresponds to the sample as quenched from 900 ºC. The second point, corresponding to the first annealing at 200 ºC shows a slight increase. We denote this region “region 0”. Between 200 ºC and 300 ºC isochronal annealing temperature the average lifetime decreases by more than 5 ps. We have denoted this region as “region I”. It should be taken into account that the spectra can be very well fitted with only one single exponential; indeed, it is not possible to decompose the spectra in regions 0 and I in more than one single exponential. Between 300 ºC and 400 ºC the slopes of the positron average lifetime curve increases noticeably. The average lifetime decreases from 179 ps to 165 ps at a constant rate. We call this region “region II”. Even though, one exponential fit of the spectra is very good in region I, the fit is not satisfactory in region II and a second component is necessary to obtain a good fit of the spectra in this region. This different behavior found in regions I and II encourages the thought that in these two...
regions something different is happening. Above 400 °C, the average lifetime remains between 167 ps and 164 ps. We call this region as “region III”.

The fact that in the as-quenched NM1 sample the average positron lifetime amounts to 185 ps and only one positron lifetime component is present in the spectrum indicates that all positrons are annihilating from one positron state, whose lifetime is 185 ps (or from several positron states with similar positron lifetimes close to 185 ps). This lifetime value is typical of positrons annihilating from vacancies in metals [13]. In order to be certain, self-consistent positron lifetime calculations for Ni, Mn and Ga vacancies (V_{Ni}, V_{Mn}, and V_{Ga}) in Ni_{2}MnGa were performed. The calculated positron lifetimes corresponding to Mn and Ga vacancies are 195 ps and 196 ps, respectively; and the one corresponding to Ni vacancy amounts to 181 ps. The calculated values show that the measured lifetime of 185 ps in the as-quenched sample corresponds to positrons annihilating in saturation from vacancies.

Figure 3 shows that $\tau_{av}$ decreases continuously in region I and, as previously cited, only one lifetime component is obtained from the spectra in this region. There are two possible explanations for this behavior: 1) the positron state from which positrons are annihilating in saturation (vacancy) is changing with temperature in region I. 2) positrons are annihilating in saturation from different types of vacancies and the value of 185 ps is the average of the different vacancy lifetimes from which positrons annihilate. The first possibility means that in the as-quenched sample only one type of vacancy is present, and with increasing temperature the vacancy turns into another type of vacancy with a shorter positron lifetime. Taking into account the theoretical calculations the second possibility would mean that in the as-quenched sample the three types of vacancies (or at least the vacancy with the shortest lifetime and one of the vacancies with the longest ones) are trapping positrons. With increasing temperature in region I these vacancies with the longest lifetimes, V_{Mn} and V_{Ga}, disappear and the vacancies with the shortest lifetime, V_{Ni} remain.

Figure 3. $\tau_{av}$ as a function of the isochronal annealing temperature for NM1 sample. The temperature dependence is divided in four regions.

Figure 4. $\tau_{av}$ as a function of the isochronal annealing temperature for NM2 sample.

In region II the average positron lifetime continues to decrease with temperature. However, the lifetime spectra can be decomposed in two components. This shows that vacancies are not trapping positrons in saturation. In other words, vacancies are disappearing with increasing isochronal annealing temperature in region II. In region III the system reaches a stable situation with small changes in the value of the average lifetime, but the spectra are still decomposed into two components, meaning that full elimination of positron traps have not been obtained.

Figure 4 shows the behavior of the average positron lifetime as a function of isochronal annealing temperature for the NM2 sample. As in the case of the NM1 sample we call region 0 the region in which there is no change in the average lifetime and spectra decomposition is not possible. In sample NM2 the region 0 reaches up to 350 °C. In this sample there is not region I, where a decrease of average lifetime is observed with no spectra decomposition possible. In region II the average lifetime decreases and a two exponential decomposition is possible. Region II
extends from 350 °C to 450 °C and region III corresponds to a stable situation and that extends from 450 °C to 600 °C.

Figures 3 and 4 show that vacancies start to eliminate at higher temperature in NM2 sample than in NM1 one. As it can be seen from the figures, region I does not exist for sample NM2. Region II is shifted by 50 °C above in NM2 sample with respect to NM1 one. This result correlates with the behavior observed in figure 2. That is, the exothermic peaks of NM1 and NM2 samples are shifted by 50 °C. This shows that the elimination of vacancies is related to the exothermic peak, which is related to the MT temperature. Taken into account that the irreversible process causing the exothermic peak is an ordering process and that ordering requires diffusion of atoms, which can be mediated by vacancies [14], one can assume that vacancies affect the MT temperature. Moreover, it is expected that different type of vacancies affect the MT in a different way.

2.3. Positron lifetime measurements in modulated samples

The behavior of the modulated M1, M2 and M3 samples (see figure 5) is very different to the one shown by the non-modulated samples analyzed above. In the M1 sample only a valley can be seen between 250 °C and 450 °C, with the overall decrease amounting only to about 3 ps. It is not possible to decompose the spectra in all the studied temperature range and the positron lifetime value of 182 ps measured below 250 °C is about the same value measured above 450 °C. So, positrons are annihilating in saturation from vacancies below 250 °C and above 450 °C. Therefore, the valley observed in the temperature range 250-450 °C cannot be understood as an elimination of only one type of vacancies.

In the M2 sample the average lifetime remains almost constant and in saturation. For the M3 sample we only have measured three points to confirm that this sample shows the same behavior as the other two. In the case of the modulated samples, the information obtained from the lifetime spectra is that the vacancy concentration is very high in all the annealing temperature range.

There exists a clear difference between positron results in the modulated and non-modulated samples. In non-modulated samples, a clear elimination of vacancies is observed, while in the modulated ones, such a decrease of vacancies is not observed at all. This means that the behavior of vacancies in these two kinds of samples is very different.

![Figure 5. \( \tau_{sv} \) as a function of isochronal annealing temperature for M1 (open circles), M2 (full circles) and M3 (squares).](image-url)
3. Conclusions

The role of vacancy type defects in modulated and non-modulated martensite transformations in polycrystalline Ni$_2$MnGa ferromagnetic shape memory alloys has been studied by measuring the effect of the thermal treatment. To be sure that the results obtained are of general validity for modulated and non-modulated Ni$_2$MnGa ferromagnetic shape memory alloys three modulated samples and two non-modulated samples were measured. These five samples cover a large range in composition.

The positron lifetime measurements show a clear difference in the behavior of positron traps (vacancies) in the modulated and non-modulated samples. In the modulated samples the vacancy concentration remains above the saturation limit in the whole temperature range. However, in the case of non-modulated samples there is a clear elimination of vacancies.

In the case of non-modulated samples, even though there is vacancy elimination, the positron lifetime behavior depends on composition. In NM1 sample, two recovery states, related to the elimination of vacancies are observed. However, in NM2 sample only one recovery state is observed.

Comparison between positron lifetime and calorimetric results indicates that vacancies affect the MT temperature.

In modulated samples a great amount of vacancies exist even at temperatures above the exothermic peak.

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