Study of Co-containing Ni-Mn-Ga by positron annihilation

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Abstract. Positron annihilation spectroscopy measurements have been carried out in the ferromagnetic shape memory alloy Ni-Mn-Ga-Co. Positron experiments have been performed at room temperature after subsequent isochronal annealing up to 600 ºC. Positron lifetime results have been compared with Differential Scanning Analysis experiments performed in the same samples. Experiments show a large variation of the average positron lifetime values with the annealing temperature of the samples, indicating a clear relation between the concentration of vacancies and the properties of the martensitic transformations of these alloys.

1. Introduction

Since the giant magnetic-field-induced strain (MFIS) 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 implement it for practical devices. The main drawbacks are the high brittleness and the low values of the martensitic transformation (MT) and 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 through the addition of a fourth element to the Ni-Mn-Ga alloy. Substituting Mn or Ga by Co martensitic transformation temperatures are higher than those found in Ni-Mn-Ga alloys [2]. On the other hand, Curie temperature increases substituting Ni by Co [3]. Therefore this quaternary alloy is a good candidate for high temperature applications under selected addition of Co. However, the effect of Co addition on the atomic order and on the vacancy density must be taken into account in order to better control transformation temperatures.

Different techniques have been used to study the properties of Ni-Mn-Ga-Co, but very little work has been performed to study the role of vacancies in the martensitic transformation. Positron annihilation spectroscopy is a very powerful technique to study vacancy-type defects in metals. We have used positron annihilation spectroscopy measurements to study the role of vacancy-type defects in the martensitic transformations of a Ni-Mn-Ga-Co polycrystalline alloy. The positron lifetime experiments have been performed at room temperature after subsequent isochronal annealing up to...
600 ºC. The positron results have been compared with calorimetric experiments performed in the same sample.

2. Experimental

Polycrystalline ingot of (Ni$_{49.5}$ Mn$_{28.5}$ Ga$_{22}$)$_{96}$ Co$_4$ (numbers indicate at. %) were prepared from high purity elements by arc melting under protective Ar atmosphere. The ingot was 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 ingot by slow speed diamond saw. These discs were used for positron lifetime measurements. Subsequent annealing treatment of 30 minutes at 900 ºC followed by quenching into ice water was performed on the alloy in a vertical induction furnace. The composition of the sample was analyzed before and after thermal treatment by energy-dispersive X-ray spectrometry (EDX) in a JSM-5610LV scanning electron microscope and it was confirmed that no compositional change took place due to thermal treatments. Differential scanning calorimetry (DSC) measurements were carried out in a TA Q100 DSC instrument to study the thermal behavior of the alloy. The sample was polished after quenching in order to ensure a good thermal contact with the equipment. The MT temperatures of the as-quenched sample were obtained from a direct measurement up to 400 ºC at a heating/cooling rate of 10 K/min. In order to observe the evolution of the MT temperatures with the heat treatment temperature, thermal cycles through the MT after heating up to different temperatures were performed at the same heating/cooling rate. All DSC measurements were performed under nitrogen atmosphere.

For the positron lifetime measurements a fast system with a resolution of 235 ps was used and a conventional $^{22}$Na source on a Kapton foil was employed as a positron source. All lifetime spectra were analyzed after subtracting a constant source contribution: a long source of 1930 ps with an intensity of 1 % and a shorter one of 400 ps with an intensity of 16 %. For the isochronal annealing in positron annihilation measurements we used the same heating/cooling rate of 10 K/min. The points in each positron lifetime curve correspond to the average obtained after 6-10 measurements. The error bars correspond to the maximum deviation of the fitted positron parameters in those measurements.

3. Results and discussion

3.1. Calorimeter measurements

Figure 1 shows the results of the DSC measurements carried out up to 400 ºC on samples quenched from 900 ºC. An endothermic peak at 124 ºC can be observed corresponding to the reverse MT (martensite-austenite). It is also worth noting the presence of an exothermic peak far above the MT. This peak could be related to processes affecting the MT [4]. 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, so the peak must be linked to an irreversible process. The presence of small endothermic peaks at temperatures above 200 ºC indicates that the reverse MT has not been fulfilled at this temperature. This stabilization of the martensite points out to defect pinning of the martensite interfaces, which could be a consequence of a high concentration of quenched-in defects in martensite [5].

In order to study the origin of the processes linked to the exothermic peak, as well as the effect they have on MT temperatures, consecutive thermal cycles from 150 ºC to 400 ºC inside the exothermic peak range were performed. These intermediate treatments only allow the partial development of the irreversible process.

Since martensitic transformations are first order phase transitions, the temperatures of their beginning and end are their characteristic parameters. The transformation of austenite into martensite (direct transformation) is characterized by the temperature Ms of the appearance of nuclei of martensitic phase in the austenitic matrix and the temperature Mp at which the transformation of the martensite ends. In figure 2, the evolution of the temperature of the MT is shown as a function of the treatment temperature. This evolution is presented in function of the parameter $\Delta$Mp=Mp-Mp$_0$, where Mp$_0$ is the temperature of the MT (position of the endothermic peak) for the sample just quenched.
from 900 ºC and Mp correspond to the MT temperature (position of the endothermic peak) for different annealing temperature. The exothermic peak in the DSC is also showed in figure 2. It can be seen that the MT of the sample first decreases up to 275 ºC and from this point increases. The maximum of the exothermic peak corresponds to the lowest MT temperature at around.

3.2. Positron lifetimes measurements

The one component fit of the experimental positron lifetime spectra is only possible up to isochronal annealing temperature of 275 ºC. For higher temperatures the $\chi^2$ is greater that 1.2. Therefore a two-component fit of the spectra is needed.

Figure 3 shows the fitted average lifetime ($\tau_{av}$) as a function of the isochronal annealing temperature. The first two points are fitted with one component, the others with two components. The $\chi^2$ of the fit is below 1.1 in all the temperature range. The average lifetime changes only a little from room temperature up to 200 ºC isochronal annealing temperature. For isochronal annealing temperature above 200 ºC a strong decrease of the lifetime occurs, until a minimum is reached at 450 ºC, for a value of around 145 ps. The decrease rate is on average of 0.16 ps/ºC. At 500 ºC a sudden increase up to 155 ps takes place. From this temperature the average lifetime remains between 150 and 155 ps and we can think that the average lifetime reaches a stable situation. The total change in the average lifetime is around 30 ps in a range of 300 ºC. All this indicates that below 275 ºC positrons are trapped in the sample in saturation. From that temperature another lifetime is necessary for a good fit of the experimental spectra. For high temperatures the fit with only one component does not give reliable results.

Results clearly show that a process of elimination of positron traps is happening during this temperature range.

Positron lifetime parameters, $\tau_1$, $\tau_2$ and $I_2$, obtained from lifetime spectrum decomposition in two components are shown in figure 4 as a function of isochronal annealing temperature. It can be seen in the figure that below 275 ºC there is saturation trapping and the lifetime after quenching from 900 ºC is 183 ps, which must correspond to the lifetime value of the positron trapping defect. At 275 ºC the saturation trapping disappears and a little short component appears. The long component remains quite constant up to isochronal annealing temperature below 450 ºC. However, at 450 ºC the long lifetime increases to around 200±5 ps.
Figure 3. $\tau_{av}$ versus isochronal annealing temperature.

Figure 4 shows the behaviour of the intensity, $I_2$, of the second long lifetime $\tau_2$ with isochronal annealing temperature, too. The intensity $I_2$ decreases from 100% at 200 °C to 52% at 450 °C. This behaviour indicates the reduction of the concentration of the associated trapping centres.

In figure 4 $\tau_1$ increases until a quite constant value of about 100 ps. This behaviour is in agreement with the one trap trapping model.

Figure 5 shows bulk lifetime, $\tau_B$, and the trapping rate $K_V$, calculated using one trap trapping model from a two-component fit:

$$\tau_1 = \tau_B / (1 + K_V \tau_B)$$  \hspace{1cm} (1)

$$\tau_2 = \tau_1 = \lambda_V^{-1}$$  \hspace{1cm} (2)

$$I_2 = K_V / (\lambda_B^{-1} \lambda_V + K_V)$$  \hspace{1cm} (3)

The value of the bulk lifetime calculated using equations (1), (2) and (3), is near constant. Indeed, it is of 136±6 ps. So, it is possible to calculate the trapping rate from 320 °C on. The trapping rate $K_V$, starts at a value of $0.11 \times 10^{12}$ s$^{-1}$ and it goes down rapidly to a constant value of around $0.005 \times 10^{12}$ s$^{-1}$. The value of 136 ps for the lifetime annihilation at the bulk is quite reasonable taking into account the lifetime annihilation bulk values for the individual bulk lifetimes of the different constituent metals in the alloy [6].

Taking into account that the trapping model works for one trap in all the studied temperature range, the results would indicate that below 450 °C there is a positron trapping defect with a life time of 183±1 ps that above 450 °C evolves into another with a life time of 200±5 ps. However, as the long lifetimes measured below and above 450 °C are within 20 ps one could explained the observed behaviour assuming that below 450 °C $\tau_2$ correspond to the contribution of at least two traps, where the defect with shorter lifetime between them is the one with the largest concentration. Above 450 °C the trap with a lifetime of around 200 ps lifetime is the one with the largest concentration. It has to be noted that the decomposition of the spectra with three components does not work.
Figure 4. Lifetime parameters $\tau_1$, $\tau_2$ and $I_2$ versus isochronal annealing temperature.

The lifetime values of $\tau_2$, 180 ps and 200 ps, associated with the trapping centres in the temperature ranges 30-450 °C and 450-700 °C respectively can be ascribed to positron annihilation lifetimes from vacancy-type defects. Indeed, taking into account that the ratio $\tau_2/\tau_B \approx 1.3-1.5$, we notice that it corresponds to the typical value for monovacancies in metals [6,7]. Therefore, the $\tau_2/\tau_B$ ratio indicates that monovacancies are the positron trapping defects. Taking into account that in the studied sample monovacancies can be of Ni, Mn or Ga and that the covalent radius of Ni is lower than the ones of Mn and Ga encourages us to associate the shorter lifetime defects with Ni vacancies and the longer lifetime defects with Mn or Ga vacancies.

3.3. Comparison between calorimetric measurements and positron lifetime measurements

As it can be inferred from the figure 2 and 3, the temperature range in which the MT temperature ($\Delta$Mpt) changes correspond to the temperature range in which the average lifetime decreases. It extends from 200 °C to 400 °C. Up to 200 °C there are no appreciable changes neither in $\tau_v$ nor in $\Delta$Mpt. Above 200 °C, $\tau_v$ decreases at the same time that $\Delta$Mpt begins to decrease. At 300 °C $\Delta$Mpt increases while $\tau_v$ is still decreasing. At 400 °C the increase of $\Delta$Mpt stops and $\tau_v$ reaches a static value of about 150 ps. This suggests that the decrease of vacancy concentration in the alloy could be related with the martensite transformation of NiMnGaCo. The decrease and subsequent increase in the
MT temperature, figure 2, suggests the presence of more than one process. One of the processes is responsible for the increase of $\Delta M_p$ and the other one for the decrease of $\Delta M_p$. One of these processes can be the elimination of vacancies. The other one can be associated to another vacancy type defect or to an atomic reordering process [4].

Figure 2 and 3 shows that the exothermic peak in the DSC and the decrease in the lifetime happen in the same temperature range. This temperature range is also the same as the temperature of the MT ($\Delta M_p$) change. It can indicate that the elimination of vacancies is related with exothermic peak and this would influence the change in the MT temperature.

4. Conclusions
The role of vacancy-type defects in the martensitic transformation of Co containing Ni-Mn-Ga polycrystalline alloy, (Ni$_{49.5}$ Mn$_{28.5}$ Ga$_{22}$)$_{96}$ Co$_4$, has been studied measuring the effect of thermal treatment on positron lifetime spectra.

By means of the trapping model a bulk lifetime of 136±6 ps has been obtained for the studied alloy.

The positron trapping centres are monovacancies and at least two different types of monovacancies are needed to explain the experimental results.

The positron average lifetime decrease occurs in the same temperature range in which $M_p$ varies. This suggests that the elimination of vacancies plays a role in the martensitic transformation. The way in which they are related and the specific mechanism that takes places in the process will be the subject of future investigations.

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