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Characterization of irradiation defects using positron annihilation spectroscopy in γ-NiSb and δ-Ni_2Si intermetallic phases

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Abstract

γ-NiSb and δ-Ni_2Si phases were studied using positron annihilation spectroscopy after electron irradiation at 20 K ($E = 3$ MeV; dose, about 5×10^{18} $e^- cm^{-2}$). Isochronal spectra of the τ_m positron average lifetime and of the Doppler broadening parameter R showed the same evolution for both compounds studied. Recombination of mobile interstitials with vacancies for NiSb occurred between 100 and 250 K although nickel vacancy migration occurred at approximately 400 K and formed dislocation loops. Mobile interstitials and vacancies recombined at a temperature as low as 77 K for Ni_2Si and were accompanied by the formation of three-dimensional mixed clusters from 325 K. At about 400 K, the less stable clusters evaporated, although recovery was still incomplete at 700 K.

In addition, a study of the positron lifetime variation as a function of measuring temperature made it possible to characterize the two- or three-dimensional nature of the clusters formed during annealing.

1. Introduction

Studies of defects outside equilibrium in intermetallic compounds of simple structure, such as B2 or $L1_2$ structures, can frequently be found [1] in the literature, unlike those related to the more complicated $B8_1$ (γ-NiSb phase) and C23 (δ-Ni_2Si phase) structures studied in this paper.

The γ-NiSb phase is hexagonal (NiAs type). It is formed by the interpenetration of three hexagonal sublattices: the (α) sublattice occupied by nickel atoms, the (β) sublattice occupied by antimony atoms and the (δ) sublattice which corresponds to vacant tetrahedral sites. This phase can be described by the $Ni_{1+x}Sb$ formula (with $-0.06 < x < 0.06$ at room temperature) for which nickel interstitials are present if $x > 0$ and stoichiometric vacancies are created in the (α) sublattice if $x < 0$ [2].

The δ-Ni_2Si phase is orthorhombic ($PbCl_2$ type). It could be derived from the $B8_2$ structure with nickel atoms in (α) and (δ) sites and silicon atoms in (β) sites with the appearance of a distortion in atomic planes [3]. An important fraction of thermal vacancies is created for high temperatures in these phases on the nickel sublattice [4]. The application of Miedema's [5] theory to determine the vacancy formation enthalpy for each sublattice of both intermetallic compounds yielded

$$\Delta H_{V_{Ni}}{}^f \ll \Delta H_{V_{Sb}}{}^f \qquad \Delta H_{V_{Ni}}{}^f \ll \Delta H_{V_{Si}}{}^f$$

2. Experimental conditions

The samples used were polycrystalline. Near-equiatomic NiSb was prepared by Lyon Aleman and Co by induction melting of high purity constituent elements and Ni_2Si was prepared in the laboratory [6] by the levitation melting of high purity nickel and silicon.

After a 3 MeV electron irradiation at 20 K (using the Van der Graaff accelerator at the Centre d'Etude Nucléaire de Grenoble), which corresponds to a dose of 5×10^{18} $e^- cm^{-2}$, the positron ^{22}Na source was deposited on a 1 μm nickel foil which was sandwiched between two identical samples under liquid nitrogen into the cryostat.

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Positron lifetime and Doppler broadening measurements were performed on 0.8 mm × 5 mm × 7 mm specimens under vacuum using a conventional fast–low spectrometer with a 255 ps full width at half-maximum. These measurements were performed from 77 to 700 K. The temperature was increased in steps of $\Delta T_A = 25$ K and the samples remained at each temperature for $\Delta t = 30$ min. Positron lifetime and Doppler broadening spectra were examined at different temperatures (77 K, annealing temperature or 300 K) of isochronal anneals and special care was taken in this study to understand the positron lifetime variation as a function of the measuring temperature.

3. Experimental results

3.1. Electron-irradiated NiSb

3.1.1. Results

(i) Figure 1 shows the recovery of the positron lifetime for the irradiated NiSb (49.8 at.% Sb) polycrystalline sample. The positron lifetime spectrum presents a single lifetime component; however, an analysis of the lifetime spectrum by means of two lifetime components cannot be excluded as the variance was not perfect [4].

(ii) The average positron lifetime spectrum appeared in two steps: the first at 77–250 K and the second at 400–600 K. The average lifetime τ_m anneals out in these ranges during the isochronal annealing treatment. Complete recovery was achieved above 600 K where τ_m is equal to τ_{bulk} in perfect NiSb. Between 250 and 400 K, τ_m remained constant.

(iii) The measurement temperature coefficient $\Delta\tau_m/\Delta T_{measure}$ was positive at the beginning of annealing and suddenly became negative at approximately 500 K.

Figure 2 shows the recovery of Doppler broadening measurements for an identical sample (Ni–49.8 at.% Sb

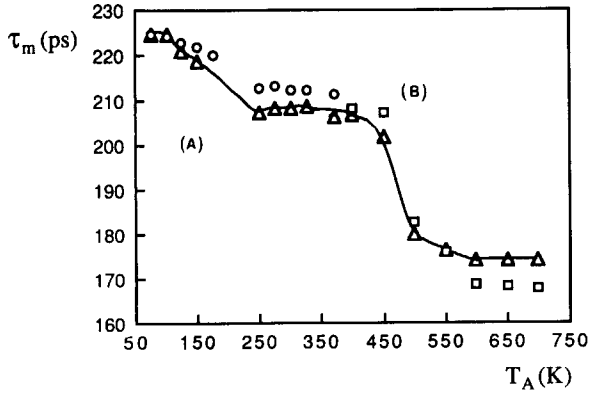

Fig. 1. Positron average lifetime as a function of the isochronal annealing temperature in Ni–49.8at.% Sb: △, measured at 77 K; ○, measured at T_A; □, measured at 300 K.

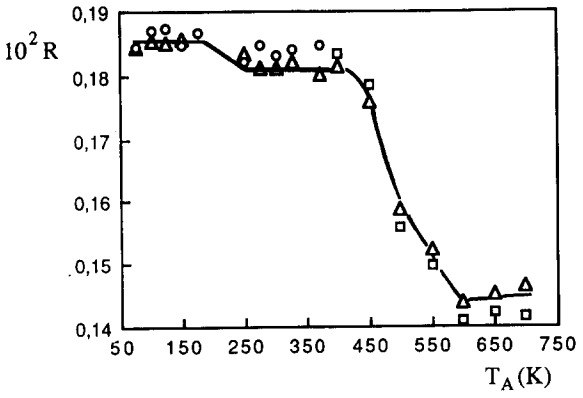

Fig. 2. Doppler broadening parameter as a function of the isochronal annealing temperature in Ni–49.8at.% Sb: △, measured at 77 K; ○, measured at T_A; □, measured at 300 K.

electron irradiated at 20 K). This spectrum presented the same behaviour as the average positron lifetime spectrum. The two spectra are thus in good agreement.

3.1.2. Interpretation

(i) The irradiation induced a clear increase in the average positron lifetime ($\tau_m = 224 \pm 1$ ps) and demonstrated the presence of irradiation-induced vacancy defects which trap positrons. A simple estimate of probabilities of creating the two vacancy types $V_{Ni(\alpha)}$ and $V_{Sb(\beta)}$ by electron irradiation can be made using the Kinchin–Pease [7] model. According to this model, the number of atoms displaced during the electronic collision is equal to the total value given by $E_{max}/2E_d$ where E_d is the energy of the displacing threshold and E_{max} is the maximum energy transferred to an atom with a mass M after frontal elastic collision with an incident electron of energy E (in this case, $E = 3$ MeV). E_{max} can be written as

$$E_{max} = 2E\left(\frac{E + m_0c^2}{Mc^2}\right)$$

Choosing $E_d = 24$ eV [8] for nickel and $E_d = 30$ eV [9] for antimony, the number of atoms displaced is three times higher in nickel than in antimony. Thus monovacancies in nickel are the predominant defect in this irradiated γ-NiSb phase.

At 77 K the value of τ_m corresponds to a 30% increase compared with τ_{bulk} (172 ps) which is the typical increase found when monovacancies are created in pure nickel or antimony. Thus $\tau_v = 224$ ps could probably be chosen for this compound. As nickel monovacancies are the dominant defect, $\tau_v = \tau_{V_{Ni}} = 224$ ps. This value is in agreement with that calculated using the lever rule and the experimental values found for pure nickel ($\tau_V = 160$ ps) [10] and pure antimony ($\tau_V = 214$ ps) [9].

(ii) The average positron lifetime spectrum was interpreted as follows. Between 100 and 250 K (stage A), a loss of some of the vacancies due to recombination with mobile interstitials at these temperatures was detected. Between 250 and 400 K, the monovacancy population was stable. The very low positive variation in the temperature coefficient (4 ps) is in accordance with what is generally observed for vacancies in metals where the variation in trapping rates as a function of temperature is almost negligible [11]. Above 400 K, vacancies migrated over long distances and were eliminated. This elimination led to agglomerates and then vacancy cluster formation. These clusters were organized during stage B, which reverses the sign of $\Delta\tau_m/\Delta T_{measure}$.

(iii) At 77 K, the presence of a positive temperature coefficient demonstrated the absence of loops in these irradiated samples, contrary to quenched samples where small loops are formed during the quench [4]. At approximately 500 K, vacancy loops were formed and immediately released, which led to a sudden inversion in the temperature coefficient. At 600 K, loops were stable and almost undetectable through measurements at 300 K.

3.2. Electron-irradiated Ni_2Si

3.2.1. Results

Figures 3 and 4 represent measurements of average τ_m positron lifetime and Doppler broadening parameter R respectively after Ni_2Si irradiation. The following conclusions can be drawn from these figures.

(i) The average positron lifetime measured at 77 K after irradiation is equal to $\tau_m = 181 \pm 1$ ps. This lifetime is greater than that measured on carefully annealed Ni_2Si reference samples.

(ii) The τ_m spectrum shows three stages: stage A_1 between 77 and 325 K where τ_m continuously decreases; stage A_2 between 325 and 400 K where τ_m increases; stage B above 400 K where τ_m decreases and reaches the value of 162 ps at $T_A = 700$ K. This value is well above that of the annealed sample (141 ps); thus recovery was not complete when measurements were stopped at 700 K.

(iii) Above 150 K, the average lifetime measured at an annealing temperature T_A is always greater than that measured at 77 K. The variation in $\Delta\tau_m/\Delta T_{measure}$ is positive.

3.2.2. Interpretation

(i) The increase in τ_m measured after irradiation is approximately 30% compared with τ_{bulk}. This type of increase corresponds to monovacancy creation in metals. Thus τ_V can be estimated at approximately 181 ± 1 ps for Ni_2Si. This value seems to be in agreement with that calculated using the lever rule and the experimental values found for pure nickel ($\tau_V = 160$ ps) [10], diluted Ni–Si ($\tau_V = 171$ ps) [10] and pure silicon ($\tau_V = 270$ ps) [12]. Considering that the number of nickel atoms is twice the number of silicon atoms in this phase, the application of the Kinchin–Pease model where the energy of the displacement threshold in silicon, $E_d = 25$ eV [13], once again yields a V_{Ni} concentration greater than that of V_{Si}.

(ii) During isochronal annealing, interstitials (which are also created by irradiation) migrate and recombine with vacancies still immobile in stage A_1 which leads to formation of three-dimensional agglomerates where some vacancies are engaged. The disappearance of these vacancies can explain the continuous decrease in τ_m in stage A_1 up to 325 K. The increase in τ_m in stage A_2 between 325 and 400 K was confirmed on the Doppler broadening curve and can be related to vacancy migration with accompanying formation of three-dimensional vacancy clusters.

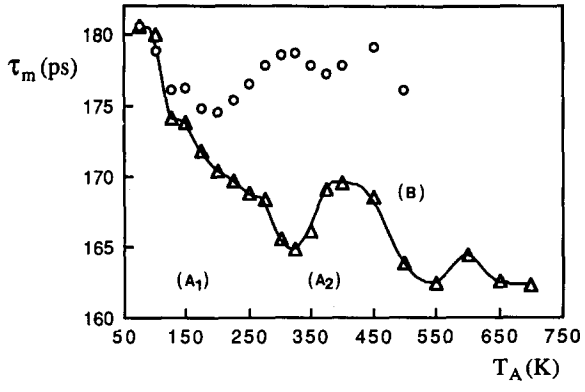

Fig. 3. Positron average lifetime as a function of the isochronal annealing temperature in Ni_2Si; △, measured at 77 K; ○, measured at T_A.

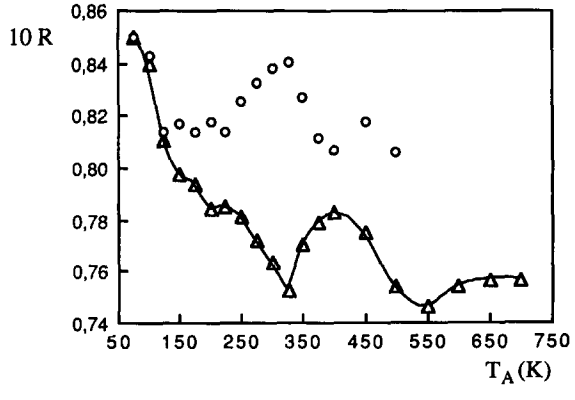

Fig. 4. Doppler broadening parameter as a function of the isochronal annealing temperature in Ni_2Si: △, measured at 77 K; ○, measured at T_A.

In stage B, the decrease in τ_m at a temperature as low as 400 K is probably linked with the evaporation of the less stable clusters and thus the liberation of vacancies which are rapidly eliminated under these temperatures. However, cluster removal is not complete as $\tau_m \neq \tau_{bulk}$ at 700 K. This result is in contradiction to those found for quenched Ni_2Si where $\tau_m = \tau_{bulk}$ at 700 K [4]. This could be explained by the fact that clusters formed during quenching and those formed after irradiation are different. In addition to the vacancy clusters, which are the only clusters found after quenching, mixed clusters can be found after irradiation which contain both vacancies and interstitials [14]; they could be more stable than pure vacancy clusters.

(iii) Unlike the results for irradiated NiSb, the variation in the temperature coefficient $\Delta\tau_m/\Delta T_{measure}$ was always positive which clearly demonstrates the absence of two-dimensional secondary defects. The formation of three-dimensional vacancy clusters is confirmed by the increase in τ_m during stage A_2 which corresponds to vacancy migration. At the end of annealing, stable three-dimensional clusters are always detected.

4. Conclusion

4.1. Interpretation of spectra

4.1.1. NiSb

The interpretation of isochronous spectra obtained by positron annihilation spectroscopy (PAS) confirms the mobility domain of V_{Ni} vacancies below 400 K in agreement with results obtained on quenched NiSb samples studied using PAS [15] and differential scanning calorimetry (DSC) [16] where only V_{Ni} are considered. Furthermore, at low temperatures, the stage situated between 100 and 250 K corresponds to the recombination of mobile interstitials with vacancies. The value $\tau_m = 224 \pm 1$ ps probably represents the average positron lifetime for a nickel monovacancy in NiSb.

4.1.2. Ni_2Si

The isochronal anneals performed confirm V_{Ni} monovacancy migration below 350 K with the formation of accompanying three-dimensional clusters, in agreement with results obtained on quenched Ni_2Si using PAS and DSC [4]. Furthermore, the fact that $\tau_m < \tau_{bulk}$ at 700 K probably indicates the presence of mixed clusters together with pure vacancy clusters. In this compound, the monovacancy lifetime is 181 ± 1 ps in accordance with the lever rule.

4.2. Measurements of $\Delta\tau_m/\Delta T_{measure}$ variation

In addition to the properties of nickel vacancies in NiSb and Ni_2Si, it was shown that information on the nature of clusters found in intermetallic compounds after irradiation could be gained by measuring the $\Delta\tau_m/\Delta T_{measure}$ temperature coefficient.

4.2.1. NiSb

A negative temperature coefficient variation could be explained by positron trapping and detrapping into two-dimensional dislocation loops where the positron binding energy is probably very small as suggested by recent theoretical calculations of positron states in dislocations [17] and analysis of positron annihilation in some metals [18]. However, a more detailed and quantitative understanding of dislocation-type defects in NiSb compounds calls for further careful measurements of the temperature-dependent positron lifetime.

4.2.2. Ni_2Si

The positive value of the $\Delta\tau_m/\Delta T_{measure}$ variation could be due to strong positron trapping by three-dimensional clusters (small cavities in this case) with high positron–cavity binding.

5. Summary

To sum up it has been shown that for irradiated NiSb and Ni_2Si compounds (1) the behaviours of nickel vacancies investigated by means of positron lifetime and Doppler broadening measurements are in fair agreement with DSC and PAS annealing curves corresponding to quenched samples [4, 15, 16] and (2) the sign of the measured temperature coefficient is directly linked to the nature of the clusters—it is positive for cavities (three-dimensional clusters) and negative for dislocation loops (two-dimensional clusters).

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