111 Cd Time Differential Perturbed Angular Correlation Study of Deformed Ni

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Using a time differential perturbed angular correlation (TDPAC) method with 111 In which decays to 111 Cd, the lattice defects induced by cold rolling in Ni metal at 77 K have been studied by the magnetic hyperfine fields observed at the 111 Cd probe nuclear sites. To investigate the dependence of annealing temperature, we have measured TDPAC spectra at 298 K during 1 hour isochronal annealing up to 1273 K in 7%H2 gas atmosphere. After 1273 K annealing, only one component which shows $\omega = 98.0 \pm 0.5$ Mrad/s corresponding to magnetic hyperfine field of 6.68 $\pm$ 0.02 T has been observed at 300 K. This frequency is interpreted as a hyperfine field at 111 Cd nucleus which occupies substitutionally the Ni lattice sites. We have also investigated the interaction between probe nucleus and lattice defects from the measurements of 111 Cd TDPAC spectra. After deformation, distinctive changes have not been observed. But after 473 K annealing, 0.60 $\pm$ 1.03 Mrad/s corresponding to magnetic hyperfine field of 2.77 $\pm$ 0.07 T was observed in addition to the component originating from the substitutional 111 Cd atoms. This frequency seems to be due to the component from the trivacancy trapping site. Because 111 In -- V3 site might transform immediately to 111 In -- V4 complex, and shows the cubic environment. This component disappeared after annealing above 873 K, and after 1273 K annealing the spectrum completely returned to the original substitutional 111 Cd spectrum before the cold rolling.

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1. Introduction

Over the past few decades, a time differential perturbed angular correlation (TDPAC) has been recognized as an useful method for studying the trapping and detrapping of the lattice defects with probe atoms in metals.1–4) 111 In isotope is the most famous nucleus for TDPAC measurements in the study of material science and has a suitable mean lifetime at intermediate state $\tau_N = 85.0$ ns. It is expected that 111 In probe atoms implanted into Ni can trap the lattice defects by annealing. Especially vacancies in Ni might be trapped by 111 In probe atom because of its large atomic radius. When the vacancies associate with 111 In probe atom, the electric field gradient (efg) at 111 Cd nucleus, which decays from 111 In, is induced by the non-spherical charge density distribution around the probe atom. Different defect configurations (e.g. single vacancy, divacancy, interstitial, etc.) produce different efgs, and therefore they can be distinguished by TDPAC method.

Several studies have been made on the defect migration and annihilation in 111 In-doped Ni4–6) and the characterization of defects which migrate in resistivity recovery stage III has been reported. This paper is intended as an investigation of which type of vacancies can interact with 111 In.

111 Cd TDPAC studies of the vacancy migration are often compared to the isochronal resistivity recovery experiment illustrated for electron-irradiated Ni in Fig. 1.12) The behavior of defects in stage III can be explained by the free migrations of mono- or di-vacancies, leading to the formation of vacancy clusters.

Table 1 shows the defect recovery models in Ni from resistivity recovery experiment, which is summarized by Schilling and Sonnenberg.1,8) This vacancy character appears to be strongly supported for most fcc metals. However, this description of the characterization of vacancies does not take into account the existence of impurities. The interaction between impurities and defects can alter the behavior of vacancies in stage III.

In this investigation, we have performed two different experiments concerning 111 Cd TDPAC in 111 In doped Ni. At first, we measured annealing temperature dependence of 111 In for Ni metal in annealing temperature range 873 K $< T <$ 1273 K and measured 111 Cd TDPAC at room temperature in order to know the behavior of 111 In doped Ni metal and to de-
termine the hyperfine interaction parameters at $^{111}$Cd nucleus dissolved substitutionally in fcc Ni matrix. The second, lattice defects have been induced by cold rolling in Ni metals at 77 K and the defects association with $^{111}$In impurity in Ni have been discussed from the hyperfine interactions observed at the $^{111}$Cd nucleus.

2. Experimental

The TDPAC measurements were performed with the well-known 171.3–245.4 keV $\gamma$-$\gamma$ cascade successively emitted from $^{111}$Cd, using a conventional four detectors arrangement in a plane at 90° angular separations. XP20Q photo multiplier mounted with BaF₂ scintillator were used. The coincidence spectrum is expressed as follows

$$N(\theta, t) = N_0 \exp \left(-\frac{t}{\tau_N}\right) W(\theta, t)$$

(1)

where $W(\theta, t)$ represents the time-dependent angular correlation, $\theta$ is the angle between the detectors and $\tau_N$ is the mean life of intermediate nuclear level of $^{111}$Cd.

For randomly oriented interaction, it can be assumed that

$$W(\theta, t) = A_{22} G_{22}(t) P_2(\cos \theta)$$

(2)

where $G_{22}(t)$ is the perturbation factor and the terms with $k > 2$ can be neglected. For $I = 5/2$ state of $^{111}$Cd under magnetic dipole interaction, $G_{22}(t)$ is expressed as

$$G_{22}(t) = \frac{1}{5} \left\{ 1 + 2 \cos(\omega_L t) + 2 \cos(2\omega_L t) \right\}$$

(3)

with $\omega_L = g\mu_N H_{int}/\hbar$ where $g$, $\mu_N$, $h$ are ordinary physical quantities. If an electric quadrupole interaction exists for $I = 5/2$ state of $^{111}$Cd, $G_{22}(t)$ has the form of

$$G_{22}(t) = \frac{1}{5} \left\{ 1 + \left( \frac{13}{7} \right) \cos(\omega_L t) + \left( \frac{10}{7} \right) \cos(2\omega_L t) \right\}$$

$$+ \left( \frac{5}{7} \right) \cos(3\omega_L t)$$

(4)

with $\hbar\omega_L = (3/20) eQ V_{zz}$. Here $Q$ is the nuclear electric quadrupole moment and $V_{zz}$ is the principal axis component of the electric field gradient tensor. The $\omega_L$ and $\omega_0$ are the Larmor frequency and the quadrupole frequency, respectively. To derive the directional anisotropies the perturbation function $R(t)$ is defined as

$$R(t) = \frac{2[N(180°, t) - N(90°, t)]}{N(180°, t) + 2N(90°, t)} = A_{22} G_{22}(t).$$

(5)

The advantage of $^{111}$Cd TDPAC study on ferromagnetic metals like Ni is that strong magnetic fields exist due to the magnetic moment of Ni and usually a large transferred hyperfine field interacts with the probe nuclei which are specific of the environment around the probe nuclei. Further experimental details of the TDPAC technique may be found elsewhere.\(^{5,10}\)

3. Experimental Results

3.1 Annealing temperature dependence

First of all, we have to confirm where the $^{111}$In atoms are actually dissolved into Ni metal by annealing at 1273 K. Therefore, we calculated the diffusion length, using a diffusion coefficient which is described as follows

$$D = D_0 \exp \left(-\frac{E}{k_B T} \right)$$

(6)

with $D_0$ is called preexponential coefficient and $E$ is the activation energy.

The diffusion length is expressed using diffusion coefficient $D$,

$$x = \sqrt{Dt}.$$  

(7)

Gust et al.\(^{11}\) reported the diffusion coefficient and activation energy that were obtained by doping Indium impurities into Ni single crystal were determined to $1.26 \times 10^{-4} \text{m}^2/\text{s}$ and 251 kJ/mol, respectively. The calculated diffusion length is 5.3 μm after accumulating 873, 1073 and 1273 K for 1 hour annealing. Since our sample is 6 × 6 × 0.5 mm$^3$ in size, $^{111}$In diffusion length is nearly equal to 5.3 × 10$^{-6}$ m, in which 1.73 × 10$^{19}$ Ni atoms exist. Considering that the $^{111}$In activity is about 2 MBq at the beginning of the measurement, it is estimated that each $^{111}$In nucleus is located per 10$^{13}$ Ni atoms, which seems that $^{111}$In nucleus is completely isolated and does not show any mutual interaction in Ni metal.

Sample consisted of the 6 × 6 × 0.5 mm$^3$ electrolytic Ni foil, whose major impurities are 0.003%Cu, 0.005%Fe and 0.003%C. The carrier-free $^{111}$In about 2 MBq in HCl solution were doped by dropping on the foil and diffusing at 1273 K for 1 hour in Ar + 7%H₂ gas atmosphere using infrared image furnace. The concentration of impurities is overwhelmingly large compared to that of probe nuclei. These impurities cannot be trapped by probe nuclei because their binding energies are smaller than those of atomic vacancies. In addition, it can be assumed that the probability that the impurities are trapped by probe nuclei is low due to the small concentration of impurities in Ni even if the concentration of probe nuclei is lower, though we need to compare the TDPAC experiment using high purity Ni.

After rinsing the sample in acetone solution for about 1 minute to remove surface $^{111}$In activity, we investigated annealing temperature dependence of $^{111}$In for Ni metal in annealing temperature range 873 K < $T$ < 1273 K and mea-
111 Cd Time Differential Perturbed Angular Correlation Study of Deformed Ni

The obtained spectra were shown in Fig. 2 together with the power spectra Fourier transformed by using a maximum entropy method.

The TDPAC spectrum, which was obtained for the specimen without any annealing treatment, showed the intense peak at about $\omega = 20$ Mrad/s. This frequency was very close to the nuclear quadrupole precession frequency of substitutional In ions in In$_2$O$_3$ or InCl$_3$. It seems that $^{111}$In nuclei are gradually diffusing into Ni metals after 873 K annealing because the melting point of InCl$_3$ is about 859 K. The Larmor frequency derived from TDPAC spectrum after 1273 K annealing was $\omega_L = 98.0 \pm 0.5$ Mrad/s, corresponding to the magnetic hyperfine field $H_{\text{int}} = 6.68 \pm 0.02$ T at 298 K. This frequency is attributed to the substitutional $^{111}$In in Ni with magnetic dipole interaction around the defect-free Ni. This value agrees well with that reported previously.\(^4\)

### 3.2 Lattice defects by deformation

The deformation by cold rolling produces various defects, such as atomic vacancies, dislocations, interstitials, etc. The vacancies can be produced by the interaction between dislocations. The vacancy array which is produced as a result of the interaction between dislocations resolves monovacancies, divacancies, etc.

From Fig. 1 and Table 1, the interstitials recombine with neighboring vacancies below 77 K. The interstitials, accordingly, migrate freely and recombine with vacancies at the time of deformation. We therefore speculate that the interstitials and dislocations are much fewer than atomic vacancies. While at higher annealing temperature than 400 K, a certain deviation is observed from Fig. 1(b) which suggests the recovery of dislocations, they may not be observed by TDPAC method because the probe nucleus can hardly trap them. In fact, as far as we know, the interstitials and dislocations have not ever been observed by using TDPAC or Mössbauer method. We therefore presume that the probe nucleus can trap vacancies only.

Sample was doped with $^{111}$In whose activity is about 142 kBq as described above. Deformation was performed with a thickness reduction using the roller at 77 K. Sample was sandwiched between two stainless steel plates cooled by liquid nitrogen. Lattice defects were excessively induced in Ni by the deformation of 63% reduction in thickness. The 1 hour isochronal annealing was performed between 473 K and 1273 K in order to trace the migration of the atomic vacancies.

Figure 3 shows the TDPAC spectra and its power spectra obtained after deformation at 77 K and subsequent annealing for 1 hour at the indicated temperatures.

TDPAC spectrum just after deformation shows little distinctive changes, which indicates that substitutional $^{111}$In have not trapped the atomic vacancies because they are still immobile at 77 K. The Larmor frequency obtained from this spectrum is $\omega_L = 105.5 \pm 0.8$ Mrad/s, corresponding to $H_{\text{int}} = 7.20 \pm 0.05$ T.

After annealing at 473 K, unstable species of lattice defects (e.g. single vacancy, divacancy) disappeared due to the free migration. The Larmor frequency derived from substitutional $^{111}$In significantly deviates from the TDPAC spectrum just after deformation, which seemed to be an analytical error. The remaining frequency was $\omega_{\text{rem}} = 40.60 \pm 1.03$ Mrad/s, which corresponds to very stable vacancies among lattice defects in Ni. It is obvious that environment of this site has cubic
temperature range between 285 K and 473 K. It seems that trivacancy trapping appears after 323 K annealing, the temperature which is slightly lower as compared to the previous report.\(^1\) The fraction of trivacancy gradually increases up to 473 K annealing.

Additionally, \(\omega_A = 8.5\text{ Mrad/s}\), \(\omega_B = 119\text{ Mrad/s}\) and \(2\omega_B\) was observed from this spectrum. The reason why \(2\omega_A\) was not observed is probably due to the insufficient analytical sensitivity. These frequencies can be explained by combined electric quadrupole and magnetic dipole interaction. Because both magnetic dipole interaction caused by magnetic moment of Ni matrix and electric quadrupole interaction caused by trapping atomic vacancies affect the probe nuclei as a perturbation. The fraction of \(\omega_A\) disappeared in the spectrum of 373 K annealing. To distinguish the origin of component with frequency \(\omega_A\), we have to consider the formation of various associations with \(^{111}\text{In}\), which depends on the migration energies of different species of vacancy.

Table 2 shows calculated energies of formation, binding and migration of mono-, di-, trivacancies.\(^{10}\) In this table, \(E_{fv}^1\), \(E_{fv}^2\) and \(E_{mv}^m\) represent energies of formation, binding and migration, respectively. The symbol \(n\) shows the number of vacancies. The migration energy of divacancies is lower than that of monovacancies, which is reported from the experiment.\(^{17}\) It is generally accepted that the defect configurations having higher \(n\) show the larger migration energy. We therefore can speculate that divacancies can migrate at lower temperature than monovacancies. In Fig. 4, the \(\omega_A\) frequency disappeared after 373 K annealing, although \(\omega_B\) still remains after 473 K annealing. Based on such grounds, \(\omega_A\) seems to be related to the interaction frequency of the probe nuclei which have trapped divacancy, and \(\omega_B\) to that which probe nuclei have trapped monovacancy. The latter frequency is in good agreement with the theoretical result of the interaction frequency resulting from trapped monovacancy \(\omega = 120\text{ Mrad/s}\).\(^1\)

As a result, the \(^{111}\text{In}\) is assumed to form complex with the trivacancy. We assume the following reaction occurring among probe nuclei at the 323 K annealing,

\[
^{111}\text{In} - V_2 + V_2 \rightarrow ^{111}\text{In} - V_3 + V
\]

\[
^{111}\text{In} - V_2 + V \rightarrow ^{111}\text{In} - V_3
\]

where \(V, V_2, V_3\) represent monovacancy, divacancy and trivacancy, respectively. Therefore, even if divacancy is trapped by the probe nuclei which already trap divacancy, we speculate...
that they may form tetrahedron $^{111}$In site with four vacancies.

Figure 5 shows the annealing temperature dependence of Larmor frequencies for which the probe $^{111}$Cd nuclei are occupying substitutional site or tetrahedral site.

Site fractions are shown in Fig. 6 as a function of annealing temperature. Site fractions are normalized by the amplitude of TDPAC spectrum obtained for 1273 K annealing in Fig. 4, for which we suppose that $^{111}$In nuclei are completely dissolved at substitutional site in Ni matrix. The circles in Fig. 6 are the sum of substitutional and tetrahedral $^{111}$In site. There is a sudden dip between 400 K and 500 K, though they remain almost constant over the whole annealing temperature range. This sudden dip implies the fractions trapping other vacancies, such as monovacancies and divacancies.

4. Conclusion

Using a technique of TDPAC, we investigated the annealing temperature dependence of $^{111}$In for Ni at 298 K and the defects in Ni induced by cold rolling at 77 K. Larmor frequencies observed at 298 K and 77 K were determined to $\omega_L = 98.0 \pm 0.5, 105.5 \pm 0.8$ Mrad/s, respectively. They corresponded to hyperfine field $H_{\text{int}} = 6.68 \pm 0.02$ and 7.20 \pm 0.05 T, respectively. These values are interpreted as magnetic hyperfine fields at ($^{111}$In $\rightarrow$)$^{111}$Cd nucleus occupying substitutional site of Ni.

The frequency obtained after deformation was $\omega_{L1} = 40.60 \pm 1.03$ Mrad/s, corresponding to hyperfine field $H_{\text{int}} = 2.77 \pm 0.07$ T. This value was interpreted as a magnetic hyperfine field at $^{111}$Cd in a tetrahedral $^{111}$In site trapped by trivacancy. This site appeared at the 323 K and disappeared at 873 K in isochronal annealing.

The frequencies derived from TDPAC spectrum of 323 K annealing were determined to be $\omega_A = 8.5$ Mrad/s, and $\omega_B = 119$ Mrad/s, which were attributed to the combined electric quadrupole and magnetic dipole interaction, respectively. From the migration energy of mono- or divacancy, we assume that $\omega_A$ and $\omega_B$ originate from $^{111}$In- divacancy, monocancy pair, respectively. Further investigation is needed to understand these results in detail.

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