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I. 9. ^{111}In Implantation in Iron and PAC Spectroscopy

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Introduction

Intensive study has been performed on Fe with techniques as Mössbauer spectroscopy or NMR/ON, of which principle is based on the hyperfine interactions. On the contrary, the application of PAC (perturbed angular correlation) method, another hyperfine interactions technique, to Fe is rather scarce. This is probably because of the difficulty in the specimen preparation. Namely, the most convenient PAC probe, ^{111}In , has a limited solubility in Fe and hence it is difficult to prepare Fe specimen with sufficient amount of ^{111}In by a conventional diffusion method. One of the present authors has attempted the diffusion method for Fe and Ni with several $100\mu\text{Ci}$ of ^{111}In and has found it works for Ni but not for Fe¹⁾. Although no detail of the diffusion method is reported, a good PAC spectrum has been obtained by Raghavan et al for ^{111}In (^{111}Cd) in Fe²⁾. Prior to them a Sweden group has reported a PAC result for Ni and Fe, where the specimen was also prepared by a diffusion method³⁾. Recently a Stuttgart group has reported a new method of specimen preparation⁴⁾. They have deposited an Fe layer electrolytically with ^{111}In activity and annealed it for the homogenization. The evaporation of ^{111}In during the diffusion anneal was prevented by the electroplated Fe layer. However the quality of their PAC spectrum is not so high as that by Raghavan et al suggesting that the amount of ^{111}In activity is not so high in their specimen^{4,5)}.

A Groningen group has reported a PAC result on Fe using ^{111}In probe⁶⁾. They have applied an ion implantation technique, the standard method of the specimen preparation for hyperfine interactions works, and obtained a good PAC spectrum. In their study, only the ^{111}In substitutional fraction was observed and no defect component was detected after the implantation at 80 K and subsequent annealing between 80-680 K. This result as well as the one by Stuttgart group⁵⁾ suggests that ^{111}In in Fe does not trap defects in a configuration to give rise to a unique frequency different from that of the substitutional site.

In the present work, a result of similar implantation work will be reported. The purpose is to practice the radioactivity handling in ISOL (Isotope Separator on Line at CYRIC) operation. Fe is chosen as the specimen since one can examine whether the

implanted ^{111}In is in the bulk substitutional site or other sites as surface oxide layer by comparing the PAC signal with those described above.

Experimental

Fe specimen is the Marz grade polycrystal 25 μm foil from MRC (Materials Research Corporation). Prior to the implantation it was annealed at 800 C for 3hrs in an UHV. The resistivity ratio was 1700, which corresponds to 30 at.ppm of interstitial impurities as carbon. The specimen was placed in the ISOL collector chamber for the implantation. A shield with a slit was placed in front of the movable specimen holder to prevent the specimen is exposed to the beams other than ^{111}In such as Ar or ^{115}In beams.

600 μCi of $^{111}\text{InCl}_3$ solution was dried with quartz fiber and placed in a crucible for Dan-Physik 910 type ion source. The accelerating voltage was 40 keV and the implantation was performed at RT (Room Temp.). The electrical current of several nA at AMU (Atomic Mass Unit)=115 was used for the calibration of the AMU meter of the ISOL. This current is from the trace amount of the natural In (^{115}In : 95.7, ^{113}In : 4.3 %) in the $^{111}\text{InCl}_3$ solution probably used as a carrier for the isotope separation. After 3hrs of implantation at AMU=111, 2 μCi of ^{111}In was implanted into the specimen, which is reasonably high to obtain several PAC spectra. The implantation efficiency (=implanted activity/charged activity) of 0.3 % in the present is comparable with the reported one.⁷⁾

PAC spectrum was measured at the room temperature by 3-detectors set up with 2" NaI detectors placed at 6 cm from the specimen. No magnetic field was applied during the measurement. After the measurement of the as-implanted state, the specimen was annealed for 1.5 hrs at 200, 400 and 600 C in a vacuum of 10^{-7} Torr.

Result.

Figure 1. shows the PAC spectrum of ^{111}In in Fe in the as implanted state and after the annealing. Despite the expected high density of the radiation damage after the implantation, a modulation pattern with the period of 11nsec is observed even in the as implanted state. This period shows a good agreement with those described above (Table 1) and proves part of the implanted ^{111}In are at the substitutional site. After the annealing at 200 C, the modulation pattern becomes clearer suggesting some part of the damage has annealed out. At 400 C, some change is observed in the modulation pattern. Further analysis is necessary to elucidate the cause of the change. At 600 C, the activity in the specimen was found to decrease. Part of ^{111}In were desorbed from the specimen and found to deposit on the wall of the furnace tube. The low activity results in the poorer quality of PAC spectrum after the 600 C annealing.

Discussion

(i) Amplitude of the Modulation Pattern

Table 1. summarizes the amplitude of the modulation in Fig.1 together with those by others. The amplitude is found lower for the implanted specimens than the diffused specimens.

Theoretical expression for the PAC spectrum in a static magnetic field vertical to the detectors plane reads as eq.(1)⁸⁾,

$$W(\theta, t, B) = 1 + \sum_N b_N \cos N(\theta - \omega_B t) \quad (1)$$

where θ is the angle between the start and stop detector, $\pi/2, \pi$, in the present. b_N is the amplitude and given as eq.(2) and (3) for $^{111}\text{Cd}(^{111}\text{In})$.⁸⁾ $\omega_B = -g\mu_N B/\hbar$ is the Larmor precession frequency. (ω_B is expressed as ω_L in some references.)

$$b_2 = (3/4)A_{22} + (5/16)A_{44} / (1 + (1/4)A_{22} + (9/64)A_{44}) \quad (2)$$

$$b_4 = ((35/64)A_{44}) / (1 + (1/4)A_{22} + (9/64)A_{44}) \quad (3)$$

With $A_{22} = -0.176$ and $A_{44} = -0.0014$, $b_2 = -0.132$ is obtained with negligible b_4 . For the present arrangement of detectors, the spectrum $R(t) = (W(\pi, t) - W(\pi/2, t)) / (W(\pi, t) + W(\pi/2, t))$ simply reduces to the following equation (4);

$$R(t) = b_2 \cos 2\omega_B t \quad (4)$$

Although this expression is only an approximation for the present unpolarized specimen (no external magnetic field), it will suffice to discuss the fraction of ^{111}In in the substitutional site.

The values of the amplitude (0.13-0.14) in the specimens prepared by diffusion are close to the calculated value of b_2 . This shows that almost all of ^{111}In are at the substitutional site in the diffused specimens. On the contrary, only 1/3-1/2 of them are at the substitutional site in the implanted specimens. The rest of them seems to be at the sites where no magnetic field is present or with a broad distribution of the field. Since the reduction takes place only in the implanted specimen, one may speculate it is caused by the damage caused by the ^{111}In implantation. So in the next section we will discuss the ^{111}In and damage distribution in implanted Fe based on a simulation program TRIM⁹⁾.

(ii) The distribution of ^{111}In and the damage after the implantation.

The result of TRIM for 40 keV ^{111}In ions in Fe shows the ^{111}In is distributed as almost a Gaussian, of which maximum is at about 100 Å from the surface and of which FWHM is 120 Å. The number of the implanted ^{111}In is calculated as $2.6 \times 10^{10}/\text{cm}^2$ from the measured activity of $2\mu\text{Ci}$ and the implanted area. If the Gaussian distribution is

approximated by the square distribution of which width is 120 Å, the FWHM of the Gaussian, the average concentration of ^{111}In is estimated as $^{111}\text{In}/\text{Fe}=2.4\times 10^{-7}$. Namely, the concentration of the probe atom ^{111}In is quite low for the case of the activity implantation. TRIM also shows the damage is distributed as a Gaussian, of which center is at 70 Å from the surface and FWHM of 125 Å. The number of Frenkel pair produced per one incident ion is 600/ion (named as vacancies/ion in TRIM). The average concentration of Frenkel pair produced is therefore $600\times 2.4\times 10^{-7}=1.4\times 10^{-4}$. In the case of the experiments where the implanted ions are used as the probe as PAC or RBS for the probe atom, this average value, however, should not be used as the damage concentration. In the case of the implantation of the heavy ion as ^{111}In , the damage is quite localized as shown by the 125 Å FWHM of the damage distribution for ^{111}In in Fe. Also the implanted ^{111}In atoms are present in this damaged zone as shown by the center of the damage distribution (70 Å) is very close to that of ions (100 Å). So let us estimate the local defect concentration in the damaged zone produced by one incident ^{111}In ion. Here we approximate the damaged zone as a sphere of which radius is the half of the FWHM of the damage distribution (125/2 Å) by TRIM. The number of Fe atom in the sphere is 8.4×10^4 . Since 600 Frenkel pair are produced in the sphere, the concentration becomes as high as $6\times 10^2/8.4\times 10^4=10^{-2}$, almost two order of magnitude higher than that of the average value. It should be noted this high concentration of the damage is always associated with each implanted ^{111}In ion. This is called correlated damage and should always be taken into account when an experiment is performed using the implanted ions as the probe. Such an example has been reported by one of the present authors¹⁰). Of course this high concentration of damage can not be accumulated when the implantation temperature is high enough for the Frenkel pair to recombine. However, the recombination is always not perfect and vacancy (interstitial) clusters or voids are left in the damaged zone. So it is likely part of the ^{111}In are incorporated in the clusters or voids where no or a distribution of hyperfine field is present. This may explain only part of ^{111}In are observed in the substitutional site in the implanted specimens. At present, however, no theoretical information is available for the hyperfine field in voids or clusters in Fe. Further analysis of the present result as well as similar experiments on Fe alloys are now in progress.

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Table 1. Summary of PAC spectrum measurements in Fe.

Period* (ns)	Amplitude	Method of Preparation	Treatment	Ref
12 1**	--	Diffusion	As Diffused	[3]
11.0***	0.14	Diffusion	As Diffused	[2]
11.1	0.13	Diffusion	As Diffused	[4]
13.3	0.07	Diffusion	e-irrad.at77K	[5]
11.3	0.07	Implanted at 77K	As-implanted	[6]
11.2	0.03	Implanted at RT	Present	

*In ref.[2, 3, 4], the spectrum is given as $\cos(\omega_L t)$, which should read as $\cos(2\omega_L t)$, where ω_L is the Larmor frequency. The selection rule for the γ correlation is $k+N=\text{even}$ and $k=\text{even}$ for $^{111}\text{Cd}(^{111}\text{In})$. (ref. [8])

**The absolute amplitude is not given in ref.[3]

***The time scale of Fig. 2 in ref. [2] is incorrect. The value cited in their text (5.5 ns) is twiced in the table.

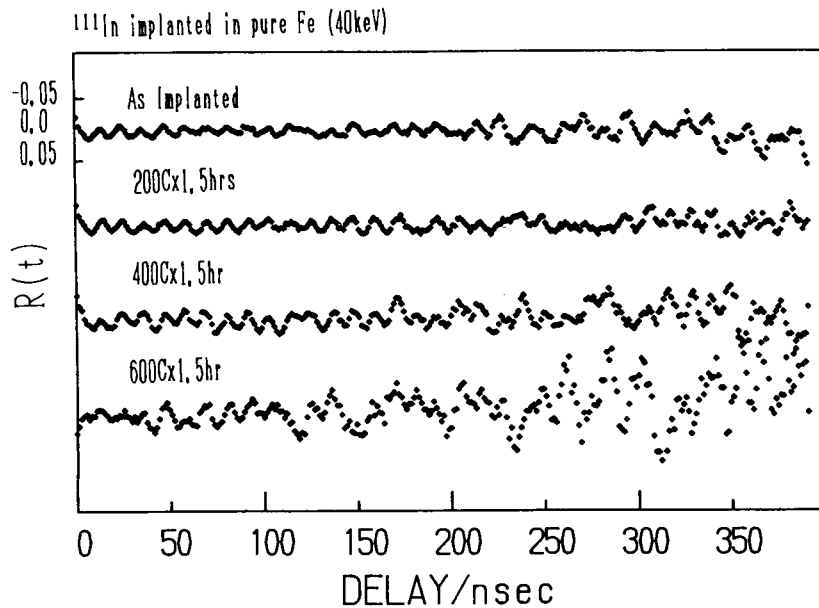


Fig. 1. PAC spectra for ^{111}In implanted in pure Fe at RT (As-Implanted) and annealed at 200, 400, 600 C for 1.5 hrs. Measurements at RT.