PAC Spectroscopy of Ni-Substitutional Alloys

I. 5. PAC Spectroscopy of Ni-Substitutional Alloys

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Introduction

In a previous report on Ni-Cu alloy, a reduction of the hyperfine field at ^{111}In at the Ni substitutional site has been reported[1]. This is interpreted as due to the substitution of one of the nearest neighbor 12 Ni atoms to ^{111}In by a non-magnetic Cu atom. Also the hyperfine field change upon alloying was calculated with the assumptions that the alloying element distributes randomly in Ni lattice and the hyperfine field reduction is proportional to the number of the non-magnetic atoms in the nearest neighbor sites.

In the present, a similar work has been extended to several Ni alloys.
The alloying elements were;
Si(2.6,5.4,8.3),Cu(1.2,3.5,7.0),Be(1.5,5.2),Al(1.0,3.5),Ti(3.1),Mn(0.53,1.9),Mo(1.5,3.2, Ir(0.8,1.8),Nb(2.3,5.3),Ge(3.5),B(4.2,6.4),Ru(3.5),Fe(7.7),Rh(5.9),Re(3.4),Gd(2.2),Dy 1.1),Er(2.3),Sm(0.9), where the number in the parenthesis is the concentrations in atomic percent. The elements and the concentrations were chosen so as that they are soluble as an α solid solution in Ni by consulting with phase diagrams[2]. The exceptions are B,Gd,Dy,Sm and Er which are not soluble in Ni and form metallic compounds.

Purposes of the experiment are; (1) to examine the random distribution model is valid or not in the Ni substitutional alloy. (2) how the phase diagram features are reflected in the PAC spectrum and (3) to demonstrate the usefulness of the melting method.

Experimental

A high purity Ni foil ($20\times20\times0.1mm^3$) was melted with an appropriate amount of the alloying element (mostly in a powder form) with ^{111}In-chrorde solution. The details of the melting method have already been reported in ref.(3). 10-15 specimens have been prepared using one vial (1ml, specific activity 5mCi/ml) of ^{111}In solution.

The PAC spectrum was measured by a three detectors system at RT with and without a magnetic field (0.27T) vertical to the detector plane. The magnitude of the field was high enough to suppress the ω_L term to obtain $2\omega_L$ term only.

Results

Fig. 1 shows PAC Fourier spectra for several Ni alloys, where the spectrum measurements were performed with the vertical magnetic field on. As expected, the ω_L term is suppressed and only the $2\omega_L$ term is present in the spectrum. The thin vertical lines show the positions of the ω_L and $2\omega_L$ term for pure Ni for comparison.

The effect of the alloying is particularly apparent for the cases of Si or Ti. Namely, the $2\omega_L$ terms are shifted to the lower side. Since the angular frequency is proportional to the magnitude of the hyperfine field as $2\omega_L = 2\,g\,\mu_N\,H/\hbar$ in the case of the magnetic interactions, the results show that the alloying reduces the hyperfine field. Similar but smaller reductions are observed for Al and Cu and almost no reduction for Be and Mn. Also for Si, Ti, Al and Mn, the spectra are considerably broadened when compared with that of pure Ni. This shows that the alloying causes the distribution in the hyperfine field. On the other hand for Be or Cu, almost no broadening is observed.

To examine the effect of the heat treatment, the spectrum was measured in the as prepared state (right after the melting specimen preparation) or after the quenching from 970C or 1230C to show that it is almost independent on them. Namely the states of the solutes are almost the same α solid solution after these heat treatments.

Fig. 2 shows similar Fourier spectra for Mo, Ir, Ge, Mn, B and Ru alloys. Here, the effects of the vertical magnetic field and the annealing after the melting specimen preparation are examined. First, for Ge, Mn, B and Ru alloys, the spectrum was measured with and without the magnetic field in the as prepared state. Without the field, both ω_L and $2\omega_L$ terms are observed as expected. The shift to the lower field side upon the alloying is found in both ω_L and $2\omega_L$ terms, of which magnitudes are proportional to them. This is reasonable since $\Delta\omega_L$ and $\Delta 2\omega_L$ terms are proportional to ΔH and $\Delta 2H$, respectively. This confirms that the shift upon the alloying is real.

The spectra after the annealing between 800 and 1000C for several 10 hrs are the almost the same with that of the as prepared state. This shows that an equilibrium state has already be established during the cooling after the melting and only minor redistribution of the solutes take place in the annealing.

Fig. 3 summarizes the results in Fig. 1 and Fig. 2 as well as other alloys not shown here. Here, the magnitudes and the width (FWHF) of the hyperfine field are plotted against the concentrations of the alloying elements. For most of alloys, reduction and broadening in the hyperfine field are observed and yet for some alloys almost no reduction is present. In the next section, the concentration dependence will be discussed based on a random distribution model.

Discussion

In a previous paper on Ni-Cu alloy, the hyperfine field in Ni alloys has been calculated with two simplified assumptions.

Namely,

(1) The solute atoms distribution in Ni is completely random in α phase.

(2) The magnitude of the hyperfine field at ^{111}In nucleus is reduced by N/12 with the substitution of N sites by non-magnetic ions among 12 nearest neighbor Ni sites

With the assumption (1), the probability to occupy N sites is given by a binomial distribution. With the assumption (2) together with (1), the hyperfine distribution has been calculated as a function of the solute concentration. The calculated results are shown by dotted lines in Fig. 3, where the maximum of the distribution is shown to shift to the lower side and the width is broadened with the increasing solute concentration. This is reasonable since the probability to occupy N sites increases with the concentration to give the shift. Also the overlap of the fields due to different N's gives the broadening.

Both of these predictions qualitatively show a good agreement with the experimental results for most of alloys. However, quantitatively, the experimental results show deviations from the random solution model. With comparing the calculated results, the experimental hyperfine field shift for each solute may be summarized as follows.

(1) Mo and Nb:much larger shift than the random solution model.

(2) Al,Si,Be,Ru and Ti: Larger shift than the model.

(3) Cu,Ge and Re : Slightly larger or close to the model.

(4) Mn,B,Rh,Fe,Gd and Er:Almost no shift.

For the group (1) and (2), the hyperfine field shift and broadening are much larger than the ones expected from the random model. Namely, the solute concentration near the probe ^{111}In is about 3-5 times higher than the average. This suggests that these solutes have an attractive interaction with the probe [111]In. For the group (3), the experimental results are close to the random model though the shift is usually higher than the predicted. So the solutes have almost no interaction with the probe or the weak one if any. For the group (4), B, Gd and Er form metallic compounds and hence have no solubility in Ni. So the probe ^{111}In just sees the hyperfine field of pure Ni giving no shift. Also this shows that the probe has no interactions with the compound.

Rh and Fe in group (4) do not give rise to the hyperfine shift although they form a complete solid solution with Ni. This suggests either that they have a repulsive interaction with the probe or they do not give rise to the hyperfine field change even when they are at the nearest neighbor site.

The present results give a quick survey of the effects of solutes on the hyperfine field of Ni. Theoretical study will be necessary to examine the reduction of the hyperfine field upon alloying.

References

1) Hanada R., CYRIC Annual Report-1998 (1999) 66.
2) *Binary Alloys Phase Diagram*: ed by Massalski.T.B., pub. by ASM (1986).
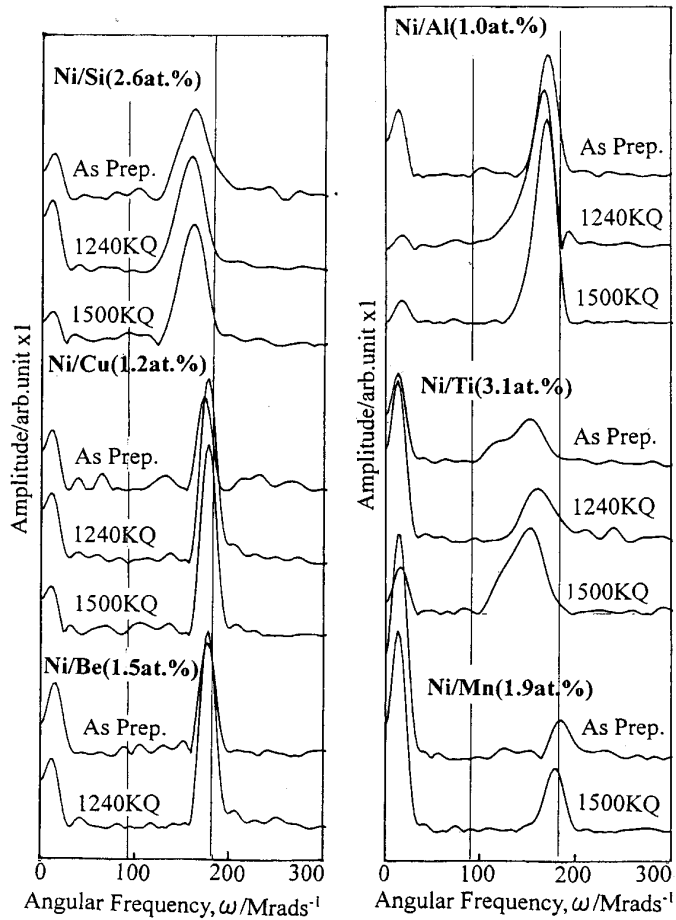3) Hanada R.,CYRIC Annual Report-1998 (1999) 49.

Fig. 1. Fourier PAC spectra for Ni-substitutional Alloys. Vertical magnetic field applied. As Prep: as melt prepared: Q: quenched.
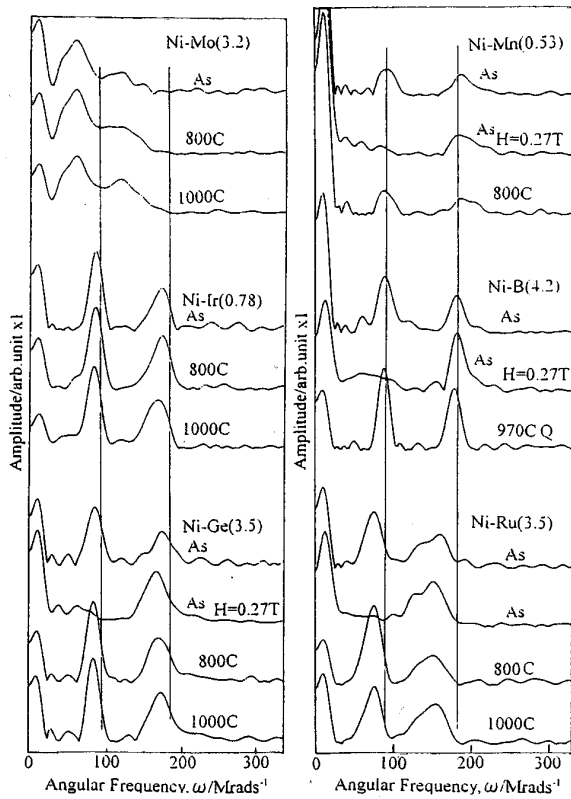
Fig. 2. Fourier PAC spectra for Ni-substitutional alloys. No magnetic field otherwise specified (H=0.27T) Annealed at the specified temperatures.
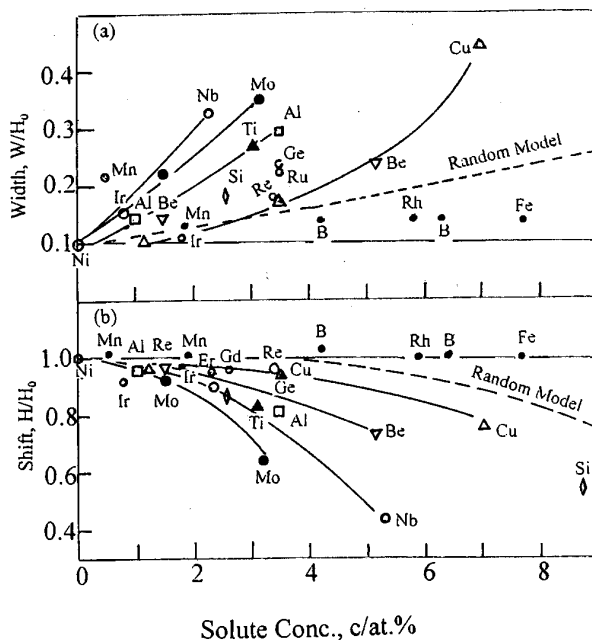

Fig. 3. The line broadening (a) and shift (b) in the Fourier components upon alloying. Normalized to the hyperfine field of pure Ni.