STRUCTURAL RELAXATION IN AMORPHOUS Fe_<40>Ni_<40>P_<14>B_<6> ALLOY STUDIED BY POSITRON ANNIHILATION AND ELECTRICAL RESISTIVITY MEASUREMENT

Supplement to Sci. Rep. RITU, A, March, 1980

STRUCTURAL RELAXATION IN AMORPHOUS $Fe_{40}Ni_{40}P_{14}B_6$ ALLOY STUDIED BY POSITRON ANNIHILATION AND ELECTRICAL RESISTIVITY MEASUREMENT

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ABSTRUCT

The Doppler broadening lineshape of 511 keV γ-ray emitted from positron annihilation, positron lifetime and electrical resistivity of the $Fe_{40}Ni_{40}P_{14}B_6$ amorphous alloy have been measured for the isochronal annealing of 0-500 °C temperature range. W-parameter of the Doppler broadening lineshape increased in two stages by annealing below crystallization temperature. These increases appear to be due to the loss of excess free volume in the amorphous alloy. The results indicate that structure of this amorphous alloy relax in two stages and excess free volume losses in the two stages

INTRODUCTION

It is well known that the structure of amorphous alloy relaxes above a specific temperature before crystallization. Although amorphous alloys have been excellent properties (mechanical and magnetic properties), these are often drastically changed by heat treatments without causing crystallization. For example, Fe-Ni based amorphous alloys obtained rapid quenching techniques become brittle after annealed at a temperature far below the crystallization temperature. Luborsky, Walter and Bacon (1,2) have found that the migration of phosphorus embrittles the amorphous $Fe_{40}Ni_{40}P_{14}B_6$ alloy at the temperature as low as 100 °C in a bending test and Auger Electron Spectroscopy. Chen (3) has studied the structural relaxation on the amorphous $Fe_{40}Ni_{40}P_{15}B_5$ alloy by Differential Scanning Calorimeter (DSC). They found that the structural relaxation occurs in two stages at about 240 °C and about 330 °C. They could not find the structural relaxation stage corresponding to phosphorus migration. Recently, a direct indication of the structural relaxation has been proposed by X-ray diffraction study (4). Egami (5) studied the structural change and kinetics of the structural relaxation in the amorphous $Fe_{40}Ni_{40}P_{14}B_6$ alloy using energy dispersive X-ray diffraction. He found that the position of the first nearest neighour peak of pair correlation function and coordination number are basically unchanged by annealing but the peaks of the pair correlation function become higher and vallys become deeper. The structural relaxation appears to be due to the loss of density fluctuation found in the liquidus or the excess free volume or structural defects in the as-quenched amorphous state during rapid quenching. Direct measurements of the loss of excess free volume have not been performed by now.

Positron annihilation studies have been made for several amorphous alloys by several investigators (6,7,8). Their results indicate that amorphous alloys contain negligible vacancy-like defects. They support the dense random packing model as the structure model of amorphous alloys. Recently Suzuki et al (9) showed that positrons are trapped into the space (for example, Bernal holes) in the amorphous Pd-Si alloy by the γ-γ angular correlation and positron lifetime measurements. Since positrons annihilate with high probability at the sites between metal ions or at a large free volume, the loss of excess free volume for structural relaxation can be detected by positron annihilation. Positron lifetime measurements have been carried out for annealed Pd-Si-Cu amorphous alloys by Chen and Chuang (10) and for annealed $Fe_{40}Ni_{40}P_{14}B_6$ amorphous alloy by Howell and Hopper (11). In this paper, we carried out a detail observation of structural relaxation on the $Fe_{40}Ni_{40}P_{14}B_6$ amorphous alloy by Doppler broadening profile, positron lifetime and electrical resistivity measurements.

EXPERIMENTS

The specimen used was amorphous $Fe_{40}Ni_{40}P_{14}B_6$ alloy (Metglas 2826 : a commercial product by Allied Chemical Company) obtained by rapid quenching techniques. Although this amorphous alloy has a complex chemical compositions, it was chosen because the annealing behavior of this alloy has been extensively studied. In positron experiments (Doppler broadening profile of 511 keV annihilation line and positron lifetime measurements) a sheet of 10 x 10 x 0.04 mm was cut from an amorphous ribbon. Isochronal annealing was performed in a vacuum of 1×10^{-5} mmHg and annealing time was chosen to be 15 minutes at each temperature. The Doppler broadening profiles of 511 keV γ-ray with positron annihilation were measured by a hyperpure Ge solid state detector at room temperature. The energy resolution of the detector was 1.15 keV for the 512 keV γ-ray from ^{106}Ru.

Positron lifetime measurements were made by the fast-slow coincidence system connected to RCA-31024 photomultiplier tubes. The typical time resolution (FWHM) of this system was 225 psec. Positron source was sandwiched between a couple of fifteen sheets of sample materials

The dimension of the sample for electrical resistivity measurements was 20 x 2 x 0.04 mm. The electrical resistivity was measured at the liquid nitrogen temperature. Since the electrical resistivity of the amorphous state is quite different from that of the crystalline state at the liquid nitrogen temperature, it is easy to detect a symptom of the crystallization in the amorphous state from the electrical resistivity measurements.

RESULTS AND DISCUSSION

The change of W-parameter of Doppler broadening lineshape of positron annihilation and the change of electrical resistivity as a function of annealing temperature are shown in Figure 1. The electrical resistivity drastically decreased by about 20 percents at 400 °C, and it monotonically decreased above 400 °C. This change shows that the amorphous $Fe_{40}Ni_{40}P_{14}B_6$ alloy starts crystallizing above 400 °C. The crystallization temperaure of this amorphous alloy by the present experiments is in a good agreement with the results of electron microscopy (12).

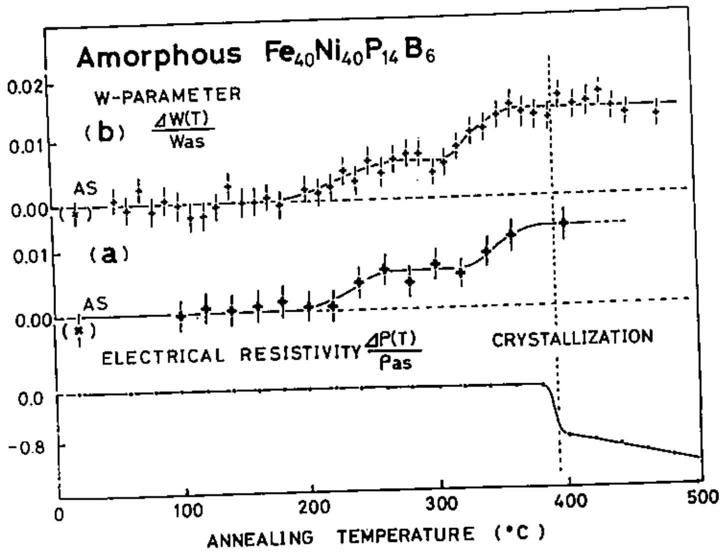

Fig.1. The change of W-parameter of Doppler broadening lineshape of positron annihilation and the change of electrical resistivity as a function of annealing temperature.

W-parameter is defined as the number of counts in 30 channels of each side tail devided by the counts in the center

200 channels of the 511 keV annihilation line. W-parameter is approximately proportional to the fraction of positron annihilating with core electrons. The change of W-parameter can be approximated as follows:

$$\frac{\Delta W(T)}{W_{as}} = - \frac{A_{V as}}{1-A_{V as}} \frac{\Delta A_V(T)}{A_{V as}}$$

Here Was indicates the W-parameter of the as-quenched sample and $\Delta W(T)$ indicates the change of W-parameter after annealing. A_V is the ratio of positron annihilating events with valence electrons to the total events. The definition of A_{Vas} and $\Delta A_V(T)$ are the same as those of W-parameter. This simple relation indicates that the change of W-parameter corresponds to the change of the fraction of positrons annihilating with valence electrons (annihilation ratio of valence electrons). In Figure 1, the two curves (a) and (b) of W-parameter are for two different isochronal annealing processes. The heating rate during the isochronal annealing for (a) was 1.3 degree per minute and that for (b) was 0.67 degree per minute. The bars indicate the standard deviations. Though the change of W-parameter is small, the reproducibility of the data is very well. W-parameter increased at about 200 °C and also at about 300 °C. These two increasing stages took place at temperatures below the crystallization temperature. These changes can be explained by the loss of excess free volume in the as-quenched amorphous alloy. Since a positron annihilates with high probability at a site between metal ions or at a large free volume, the annihilation ratio with valence electrons will be decreased by the loss of excess free volume during annealing. Therefore W-parameter increased due to the structural relaxation. The increase of W-parameter indicates the amount of excess free volume disappeared. These results indicate that excess free volume remaining in as-quenching amorphous alloy is discharged in two stages due to structural relaxation. W-parameter measurements could not be found the change by the phosphorus migration due to the annealing at the temperature as low as 100 °C (1,2).

Figure 2 (a) is the W-parameter curve after smoothing of Figure 1 (b) as a function of annealing temperature. Figure 2 (b) shows the differential curve of the W-parameter curve Figure 2 (a). The differential curve of W-parameter is related to the amount of discharged free volume during the each annealing stage. This curve has two distinguishable peaks at about 240 °C and 330 °C. Figure 2 (c) shows the temperature dependence of the difference on the specific heat capacity between as-quenched amorphous $Fe_{40}Ni_{40}P_{15}B_5$ alloy and annealed one obtained by Chen (3). These curves (b) and (c) in Figure 3 agree quite well. Consequently, the increases in the W-parameter are clearly attributed to the two distinguishable relaxation stages

Positron lifetime was also measured after heat treatment. Positron lifetimes in as-quenched state, the first relaxed state after 300 °C x 15 minute annealing and the crystalline

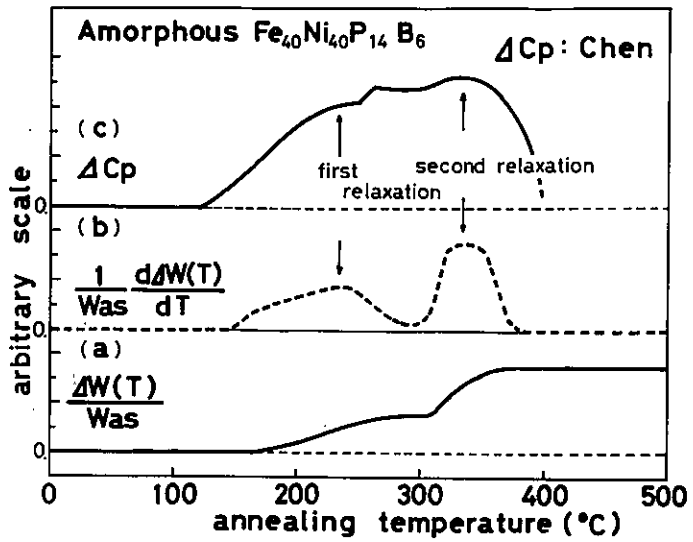

Fig. 2 (a):the W-parameter curve, (b): the differential curve of the W-parameter, (c): difference on the specific heat capacity by Chen (3)

state were 159 ± 1 psec, 157 ± 1 psec and 153 ± 1 psec, respectively. These lifetimes are obtained by one component fitting analysis except the source components. Since positrons trapped at the excess free volume have a long lifetime, the lifetime of the annealed sample became shorter than that of as-quenched sample by the loss of excess free volume. Therefore the results consist with those for W-parameter of Doppler broadening measurements. These positron lifetimes are similar to those obtained by Howell and Hopper (11)

Changes in the W-parameter during isothermal annealing are shown in Figure 3. The annealing method is the same as that of isochronal annealing. The annealing temperature was 250 °C. The W-parameter monotonically increased with annealing time and W-parameter behaved logarithmic dependence. These phenomena correspond to the first relaxation stage. Although the quantitative relation between W-parameter and concentration of excess free volume is not clear, the simple logarithmic time dependence of W-parameter implies that W-parameter or annihilation ratio with valence eletrons is a useful parameter of structural relaxation. The logarithmic time dependence has been observed in certain cases of mechanical creep (13) or structure factor (5)

Slight changes of the electrical resistivity at liquid nitrogen temperature during isochronal annealing and differential curve of W-parameter are shown in Figure 4. The electrical resistivity increased about 0.2 percent at the first relaxation stage. Above this temperature, the electrical resistivity slightly decreased. This interpretation is not

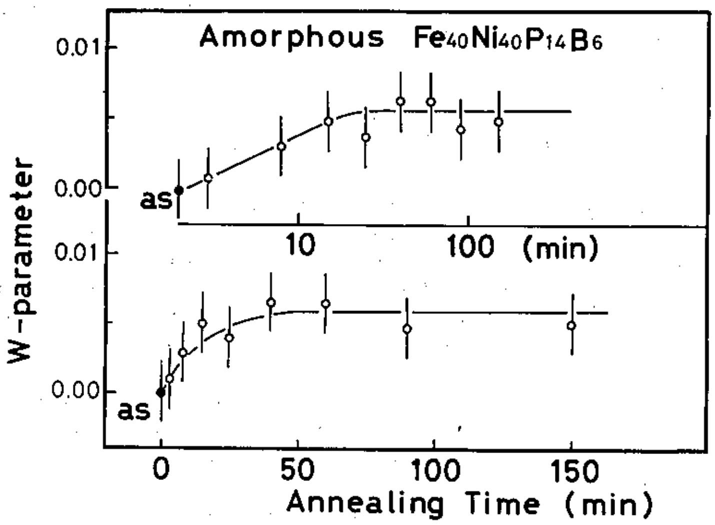

Fig.3 The change of W-parameter during isothermal annealing.

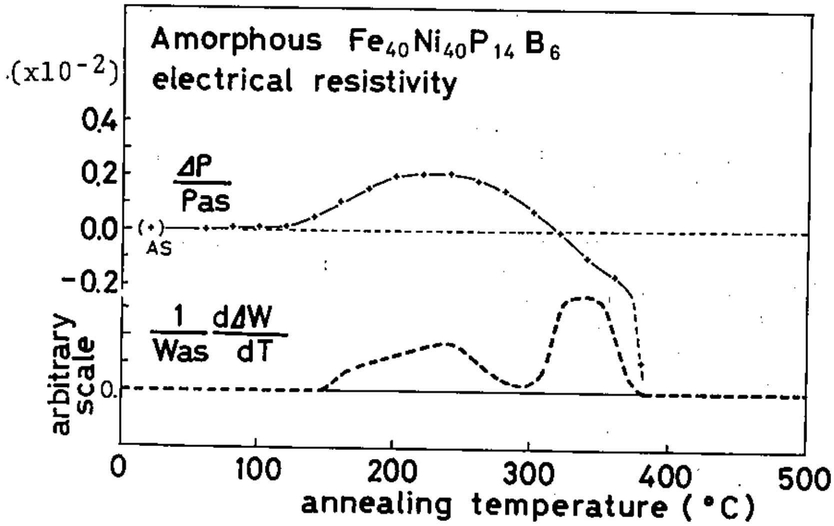

Fig.4 Changes of electrical resistivity same as Figure 1 but in expanded scale and differential curve of W-parameter.

clear, but feasibility of electrical resistivity increase at the first relaxation stage may be caused by the structure change. Wright (14) showed that the electrical resistivities of amorphous Fe and Ni are larger than those of liquid Fe and Ni respectively. Fujiwara (15) explained this experiment with a computer simulation. He indicated that a d-electron density of states at the Fermi energy and s-d hybridisation attribute the electrical resistivity using the Mott model. There are several liquid like regions in as-quenched amorphous alloys. On the other hand, after structural relaxation, annealed amorphous alloy is closer to the ideal amorphous state. By comparision of structure between the liquid and amorphous state, the increase of electrical resistivity after structural relaxation is explained by the s-d hybridisation.

The following suggestions are made with the results of X-ray diffraction study (5) and differential scanning calorimeter study (3). At the first relaxation stage, (liquid like) random configuration will be changed to the high short range ordered state with a low activation energy. Most unstable excess free volume disappear in this stage. Structure sensitive properties like the electrical resistivity or the magnetic properties change at this first relaxation stage. Chien and Hasegawa (16) and Tseng et al (17) have studied the alternation of magnetization axies of iron nuclei during heat treatments of iron based amorphous alloys with Mössbauer spectroscopy. At the second relaxations stage atomic rearrangement is not so clear. One possible explanation is the atomic rearrangement for the formation of molecular like small atomic clusters. The small cluster is constructed by Fe_3B, Fe_3P etc. These structure will be the same as those of the crystalline phase

CONCLUSIONS

The results obtained can be summarized as follows:

(1) Positron annihilation techniques are a useful method to the study of structural relaxation in amorphous $Fe_{40}Ni_{40}P_{14}B_6$ alloy and sensitive to the loss of excess free volume.

(2) W-parameter of Doppler broadened two phonon annihilation increased in two stages during the isochronal annealing below the crystallization temperature. These increases agree with the structural relaxation study of specific heat capacity obtained by DSC. These results are interpreted by the loss of excess free volume at two relaxation stages.

(3) The structural relaxation of amorphous $Fe_{40}Ni_{40}P_{14}B_6$ alloy has two stages. At the two annealing stages, excess free volume is discharged from as-quenched amorphous state by heating. At the first relaxation stage, some liquid like configuration remained in as-quenched amorphous state will be relaxed into high short range ordered state and the structural sensitive properties like electrical or magnetic properties change at this first relaxation stage.

ACKNOWLEDGEMENTS

We are deeply indebted to the International Copper Reseach Association(INCRA), the Ministry of Education, the Kurata Foundation and Jappan Copper Development Association for the Grant in Aids. We acknowledge the donation of the materials for Nippon Kokan K.K., Nippon Steel Corporation, Hitachi Ltd.,Nippon Mining Co.,Ltd.,Mitubishi Metal Co., Ltd. and Showa Denko Co.,Ltd.

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