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ATOM PROBE FIM STUDY OF AN AMORPHOUS Pd-Si ALLOY

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Abstract - The amorphous structure of Pd₈₄Si₁₆ alloy wire obtained by in-rotating-liquid spinning method from the liquid state, has been studied, in an atomic scale, by atom-probe field-ion microscopy. In the as-solidified specimen of Pd₈₄Si₁₆ alloy, whose electron diffraction pattern shows single halo ring, compositional fluctuation is found to exist in the range of 8 to 24 at% Si. The fluctuation is of the period of a few tenth nanometer, and it does not have long-range periodicity. We have discussed these experimental results with microcompositional fluctuation in terms of both amorphous structure itself and artifact effect with field evaporation.

I - INTRODUCTION

Amorphous structure has been studied intensively from experimental and theoretical points of view. Although the studies with both topological and chemical structure are necessary, most of studies have been concerned with topological structure. But recently the importance of the knowledge of chemical structure on amorphous phase has been recognized, because of easy formation and stabilization of amorphous phase by an addition of metalloïd element. Actually studies on chemical structure are being made by some techniques such as X-ray, electron and neutron diffractions, Moessbauer spectroscopy and extended X-ray absorption fine structure (EXAFS).

An atom probe field-ion microscope /1/ is powerful to study the chemical structure of amorphous alloy. It has been applied to the study of amorphous alloys of Fe₄₀Ni₄₀B₂₀, Ni₆₀Nb₄₀ and Ti₅₀Be₄₀Zr₁₀ by Haasen, Wagner and co-workers /2-4/.

In this work we selected a Pd rich Pd-Si alloy because it is one of the typical amorphous alloys, and studied chemical structure of amorphous phase, in an atomic scale, by using an atom-probe.

II - EXPERIMENTAL PROCEDURE

The Si content of the alloy in the present study is 16 at%. The alloy wire obtained by the in-rotating-liquid spinning method from liquid state /5/ was used to avoid artifact effects in a specimen preparation process such that the specimen temperature would rise on cutting of the ribbon specimen into specimen with square or circular cross section.

The atom probe analyses were performed employing our computer-controlled straight-type time-of-flight atom-probe. The detail of our atom probe is described elsewhere

/6,7/. In order to confirm amorphous state the tip-shaped specimen was examined by electron diffraction technique.

III - RESULTS AND DISCUSSION

1. Electron diffraction pattern

Figure 1 is a typical electron diffraction pattern obtained from a specimen tip of as-solidified $\text{Pd}_{84}\text{Si}_{16}$ alloy. This shows a single halo ring. The ring is intense and diffuse. This halo pattern confirms that the as-solidified specimen is in amorphous state. Dark field imaging by the halo ring was tried, but an image did not show any particular microstructure. When the as-solidified specimens were annealed for a short period of time at 563 K, their diffraction patterns changed into triple and quadruple halo rings with increase of annealing time. The details of these changes are not described here.

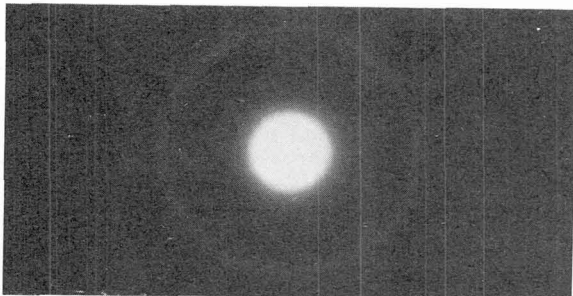


Fig.1 - An electron diffraction pattern of as-solidified $\text{Pd}_{84}\text{Si}_{16}$ alloy, showing amorphous state.

2. Atom-probe analyses

2.1. Mass spectrum

The mass spectrum of atom-probe data consists of Pd^{2+} , Pd^+ , Si^{2+} and Si^+ . The 60% of Pd are field-evaporated on the doubly charged state and the 40% are in the singly charged state, while most (94%) of Si is in the doubly charged state. Since Pd and Si peaks do not overlap each other in the spectrum, we can clearly identify the atomic species, Pd or Si.

2.2. Field-evaporation behavior of the amorphous alloy

Figure 2 is a plot of Pd ions plus Si ions detected versus the cumulative number of field evaporation pulses. This figure presents a field evaporation behavior. Pd and Si ions are detected on an atom-basis, and Pd and Si ions of the ordinate in the figure increase smoothly. So the field-evaporation of the amorphous Pd-Si alloy occurs smoothly. This suggests that the bindings between two atoms in the amorphous Pd-Si alloy are not much different among Pd-Si, Si-Si and Pd-Si in a rough evaluation because the field-evaporation is strongly related with the binding.

2.3. Si atom distribution in the alloy

Si atom distribution in the alloy, in the relatively large scale, is shown in Fig.3. It is a plot of the cumulative number of Si ions versus the cumulative number of Pd plus Si ions during continuous field evaporation in the atom-probe analysis, demonstrating a part of a run. The average slope of the figure presents the average composition. The average composition determined by the atom-probe analysis is 15.7 at%Si. This value is in good agreement with the composition (16.0 at% Si). In Fig.3 there is neither large compositional change nor any precipitate. In the early study on the amorphous structure of Pd-Si alloy, Duewez et al. /8/ made a thin foil specimen of amorphous Pd-20at%Si alloy by the gun technique or the piston and anvil

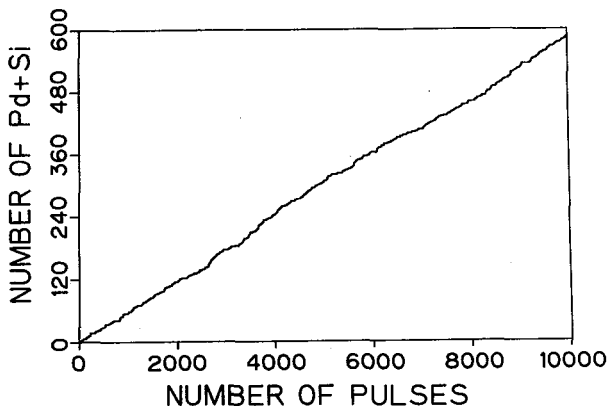


Fig.2 - A plot of Pd ions plus Si ions detected versus the cumulative number of field-evaporation pulses, showing field evaporation behavior of amorphous $\text{Pd}_{84}\text{Si}_{16}$ alloy.

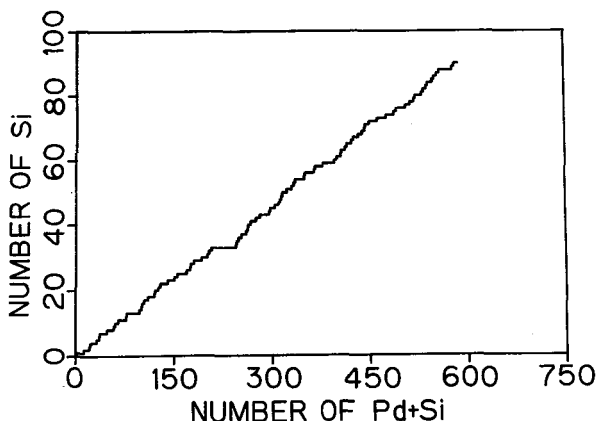


Fig.3 - A plot of the cumulative number of Si ions versus the cumulative number of Pd plus Si ions during continuous field evaporation in atom-probe analysis of amorphous $\text{Pd}_{84}\text{Si}_{16}$ alloy

technique, and observed the specimen by transmission electron microscopy (TEM). Masumoto and Maddin /9/ also observed the ribbon specimen of amorphous $\text{Pd-20at}\% \text{Si}$ alloy by TEM. Both TEM results show that the structure is quite uniform in the bright field image. The present atom probe results are consistent with their results by TEM observation in terms that amorphous Pd-Si alloys have uniform structure in the relatively large scale.

The detailed analyses of the present atom-probe data, however, indicate the possibility for existence of micro-fluctuation in Si atom distribution, as will be described. In order to examine the micro-fluctuation of Si atom distribution, the two kinds of analysis were made: (i) frequency distribution of composition of atom blocks, and (ii) auto-correlation analysis for composition profile.

Let us describe the first analysis. In the atom-probe analysis, the protruded atoms in the surface of the alloy field-evaporate and the ions going through the probe hole reach the detector. The successive detections of the ions during continuous field evaporation give the depth profile of composition in the alloy along the axis of the analyzed cylindrical region. When the sequence of the detected ions is divided into a number of blocks each of which contains n ions, where n is an integer, the composition of each block is determined. For the present analysis, various values of n were taken. Figure 4 is a depth profile of composition in the amorphous $\text{Pd}_{84}\text{Si}_{16}$ alloy for the case where the number of ions in one block is 25 ($n=25$). It is noticed that the Si concentration is not constant but fluctuates.

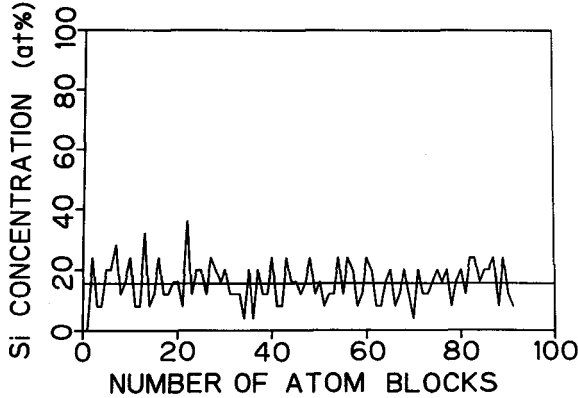


Fig.4 - A depth profile of composition in the amorphous $\text{Pd}_{84}\text{Si}_{16}$ alloy for the case where one block contains 25 ions.

Frequency distribution of composition of ion blocks obtained from the Fig.4, is shown in Fig.5. If Si atoms distribute randomly in the alloy, the distribution is binomial. However, when the present frequency distribution has been compared with the binomial distribution and has been tested by the chi-square goodness-of-fit test /10/, the probability that the present distribution is binomial distribution is 20%. This value is small, and this implies that the present distribution is different from the purely random distribution. The frequency for 16at%Si, which is the alloy composition, is relatively low, and the frequency splits into two parts: the lower side of Si concentration (8 and 12 at%Si) and the higher side (20 and 24 at%).

Frequency distributions of compositions for various values of n are obtained and then it is found the micro-fluctuation is prominent for $n=25$. The size of the cylindrical region containing detected 25 ions is 2.5 nm in diameter and 0.14 nm high. This is evaluated by the following way. The volume of one block, V is given by

$$V = m \gamma v / \eta ,$$

where m is the number of atoms existing actually in the one block, γ the detectability of the atom-probe system including the detectability of the Chevron CEMA detector, v the atomic volume, and η the packing density. Giving $n=m\gamma=25$, $\gamma=0.6/11,12/$ and $\eta=0.63/13,14/$, and using a weighted average value of Pd and Si atoms for the atomic volume v , V is obtained for the present case. Since the analysed area is evaluated to be 2.5 nm in diameter from the image, the thickness becomes 0.14 nm. Thus it has been revealed that the high and low regions of Si concentra-

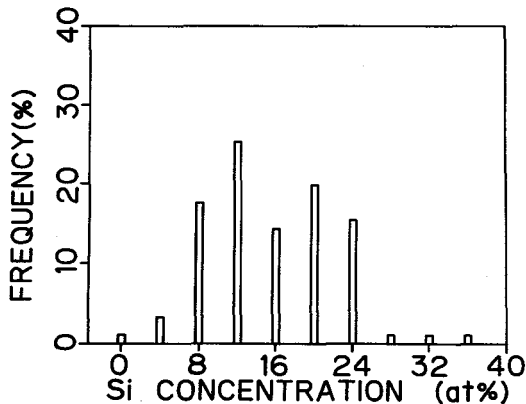


Fig.5 - Frequency distribution of composition of atom blocks in amorphous $\text{Pd}_{84}\text{Si}_{16}$ alloy, which is obtained from Fig.4.

tion exist a few tenth nanometer order apart.

In order to investigate the positional relations between such high and low regions of Si concentration, the autocorrelation analysis for the composition profile of Fig.4 was made -- the second analysis. The correlation coefficient $R(k)$ is given by

$$R(k) = [N/(N-k)] \left[\sum_{i=1}^{N-k} (C_i - C_0) (C_{i+k} - C_0) \right] / \left[\sum_{i=1}^N (C_i - C_0)^2 \right]$$

where C_i and C_{i+k} are the composition of the i -th and $(i+k)$ -th ion blocks, C_0 the average composition, N the total number of ion blocks, and k the correlation length. A plot of $R(k)$ versus k is shown in Fig.6. According to the test of the the reliability in the statistics, $R(k)$ is meaningful only for $k=1$ and 3. At $k=1$ it has the negative correlation. This means that there is a tendency to be a combination of higher and lower Si concentration at the adjacent blocks. The positive correlation at $k=3$ means a tendency to be higher (or lower) concentration of Si at every four blocks. As the depth of a block is 0.14 nm, the distance between the

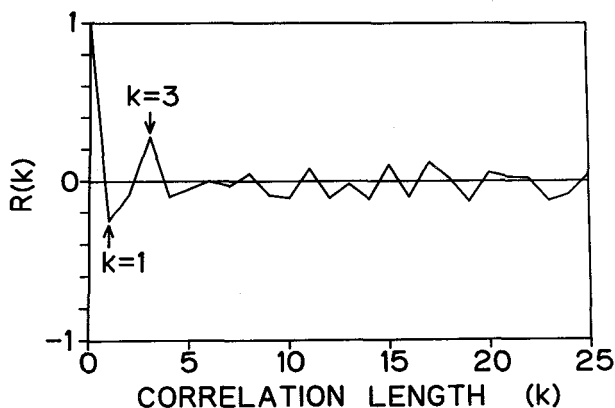


Fig.6 - An autocorrelation analysis of amorphous $\text{Pd}_{84}\text{Si}_{16}$ alloy, which is obtained from Fig.4.

higher and the following higher regions becomes about 0.4 nm. It is known that the first position crossing the k -axis, i.e., the first $R(k)=0$ in the autocorrelogram corresponds to the average particle size of precipitates if there are precipitates in the alloy. For the present case $R(k)$ crosses at the k value below one. The state of the alloy does not have any fine precipitate but has compositional fluctuation with a small wave-length. However, this compositional fluctuation does not have long-range periodicity because the autocorrelation analysis of Fig.6 does not have positive correlation at $k=6$ which is at the twice of the first positive peak.

When we consider this compositional fluctuation in comparison with the probe hole size used in the present study, some more information is obtained as described below. The probe hole size must be large enough to collect the number of atoms which is statistically reliable in one block. However, when the probe hole size is too large in comparison with the periodicity of fluctuation, the data would show only the average picture to be integrated over the whole period of the fluctuation. In the present results shown in Fig.4, Fig.5 and Fig.6, the number of atoms in one block is 25, as was described in the section 2.3, and is fairly satisfied to be large at the statistical point of view. The probe hole size is 2.5 nm as was also described in the section 2.3. This size is relatively large in comparison with the fluctuation period of 0.42 nm. If the fluctuation exists in the three dimensional mode, it is not detected because of averaging of fluctuation. The present detection of fluctuation implies that the fluctuation is in the one dimensional mode along the probed direction. Here we remember that when amorphous Pd-Si alloy is annealed, it decomposes into Pd_3Si phase and Pd rich solid solution /9/. The crystal structure of this Pd_3Si is a sort of the layered structure like an ordered alloy and has one

dimensional periodicity. Thus the microcompositional fluctuation shown in the present work might be a precursor of phase separation into Pd_3Si and Pd solid solution. Most of the Pd_3Si embryos might be oriented to the longitudinal direction of the alloy wire which is the probed direction because of temperature gradient and internal stress along the longitudinal direction of wire. It is known that phase separation has been observed in some alloy systems on annealing process of the amorphous alloys produced by quenching from the liquid state /15/. However, the existence of microcompositional fluctuation in the as-quenched state where the quenching rate of the specimen is comparable to the previous works /16/.

Before it is concluded that the above features are a genuine property of the bulk materials, the possibility for spurious results in the present atom-probe analyses must be discussed. Miller and Smith /17/ have analysed Fe-3wt%Si alloy by atom probe and found that the Si atoms were retained at the central part of (110) plane and the overall apparent level of Si was approximately three times higher than expected, although the alloy was homogeneous in the structure. Yamamoto and Seidman /18/ have also found an abnormal increase in the number of Mo atoms in the central portion of the fundamental (211) plane indexed on the basis of body centered tetragonal structure, of ordered Ni_4Mo . Miller and Smith /17/ have discussed that these phenomena may occur at the close-packed planes and they are due to migration of the solute atom on the close-packed plane because the activation energy to overcome for migration is very low in the close-packed plane. Actually (110) plane of body centered cubic structure for Fe-3wt%Si alloy and (211) plane of body centered tetragonal structure for ordered Ni_4Mo alloy are close-packed planes. However, in an amorphous structure in the present study, relatively flat portion like close-packed plane does not exist or rarely exist. Thus such a phenomenon could not occur in the amorphous structure.

In summary of the present analyses, microcompositional fluctuation of Si atoms is found to exist in the as-solidified, amorphous $\text{Pd}_{84}\text{Si}_{16}$ alloy in an atom-probe study. This implies the existence of Pd_3Si embryos.

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