# Time-differential perturbed-angular-correlation studies of the amorphous Cu-Hf alloys prepared by mechanical alloying and melt spinning

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Time-differential perturbed-angular-correlation spectra of the amorphous Cu-Hf alloys prepared by mechanical alloying and melt spinning were measured. The short-range structures in mechanically alloyed and melt-spun amorphous Cu-Hf alloys are compared from a microscopic point of view. It is seen that in the melt-spun amorphous alloy, Hf can occupy a disordered-Hf site or a site as in intermetallic-like $Cu_3Hf_2$.

## I. INTRODUCTION

Recently, the mechanical-alloying (MA) technique has been of interest for synthesizing amorphous alloys.[1,2] Up to now, amorphous materials have been prepared mainly by melt spinning, sputtering, and evaporation. Mechanical alloying, which is a solid-state process, is performed at temperatures below the crystallization temperature. This method also has a different time scale as compared with the rapid quenching. At present, the microscopic mechanism of the solid-state amorphization reaction has not been clearly understood. In addition, it is a challenging problem to investigate the short-range structure of amorphous materials which are synthesized by mechanical alloying. Recently, it has been suggested that the short-range atomic distribution might be the same in amorphous alloys prepared by rapid quenching and mechanical alloying.[3–5] This suggestion was introduced as a result of the similarities between the reduced atomic distribution function, which are determined by x-ray diffraction. Neutron scattering[6,7] and EXAFS[8,9] studies support dense random-packing models[10,11] for the structures of amorphous alloys prepared by mechanical alloying. Mössbauer spectroscopy has been used to study the amorphization mechanism induced by repeated rolling.[12,13] In order to characterize the short-range structures in the amorphous materials prepared by MA, further investigations by microscopic methods are required. The time-differential perturbed-angular-correlation (TDPAC) technique provides a way of determining the crystal-field parameters around the probe atom through the hyperfine interaction between the nuclear quadrupole moment of the radioactive ions and the electric-field gradient (EFG).[14] The crystal-field parameters, EFG tensor, $V_{zz}$, along with the asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$ at the reference atoms, provide information about the angular distribution of atoms in the local environment, which is complementary to information concerning the radial distribution function. In this study, we have measured the time-differential perturbed-angular-correlation (TDPAC) spectra of the Cu-Hf alloy after amorphization induced by mechanical alloying, and compared with TDPAC spectra of melt-spun amorphous Cu-Hf alloys. The microstructures around the probe atoms in the mechanically amorphous alloyed Cu-Hf and rapidly quenched Cu-Hf alloys are discussed.

## II. EXPERIMENT

Pure elemental powdered copper (99.9% pure, and on average less than $\sim 150\mu$m) and hafnium (99.9% pure, and on average less than $\sim 150\mu$m) were mixed to give average compositions of $Cu_{57}Hf_{43}$ powder. The sample was sealed in a tungsten carbide vial with the inner diameter $\sim 80$ mm, together with tungsten carbide balls $\sim 10$ mm in diameter under an Ar atmosphere. The mechanical alloying was carried out in a conventional ball-milling apparatus, where the rotation speed was $\sim 100$ rpm. For comparison, we prepared a melt-spun amorphous $Cu_{57}Hf_{43}$ alloy. The melt-spun specimens were fabricated in a He atmosphere in ribbon form approximately 5 mm in width and approximately 20 $\mu$m thick, by means of the single-roller technique. The diameter of the Cu roll was 33 cm and the quenching speed was adjusted by rotating at $\sim 3000$ rpm. The x-ray-diffraction-patterns were taken by means of a $2\theta$-$\theta$ powder diffractometer with Cu-$K\alpha$ radiation. Radioactive $^{181}$Hf probe atoms were produced by thermal-neutron capture [$^{180}$Hf$(n,\gamma)^{181}$Hf] in the JRR-4 reactor at the Japan Atomic Energy Research Institute. The total dose of thermal neutrons was $\sim 3\times 10^{18} n/\text{cm}^2$. The temperature of the specimen remained below 80 °C during the reaction. The experimental setup for the TDPAC measurement is a so-called fast-fast coincidence system which is composed of four

$BaF_2$ detectors with constant-fraction-differential discriminators. We can obtain two TDPAC spectra for interdetector angles $\theta=180°$ and $\theta=90°$ to be measured simultaneously. We adopted R2059(Hamamatsu) photomultipliers. The time resolution was 0.7 nsec full width at half maximum (FWHM) for both interdetector angles. We used the 133–482 keV cascade in the excited levels of $^{181}$Ta. From the TDPAC spectra $N(180°,t)$ and $N(90°,t)$, we evaluated the counting-rate ratio

$$R(t)=\frac{2}{3}\left[\left[\frac{N(180,t)N'(180,t)}{N(90,t)N'(90,t)}\right]^{1/2}-1\right],$$

which is represented as $R(t)=A_2G_2(t)$. $A_2$ and $G_2(t)$ are the angular correlation and the perturbation factors, respectively. If the EFG is unique, then $G_2(t)$ is represented as follows:

$$G_2(t)=S_{2,0}+\sum_{i=1}^{3}S_{2,n}\cos(\omega_i t),$$

where $S_{2,n}$ are tabulated parameters involving vector coupling algebra only. The crystal-field parameters are calculated from the transition frequencies $\omega_i$. The transition frequencies are obtained by a spectral analysis of the TDPAC spectrum $R(t)$.

## III. RESULTS AND DISCUSSIONS

The x-ray-diffraction patterns of the $Cu_{57}Hf_{43}$ sample for ball milling are shown in Fig. 1. It is evidently seen that Bragg peaks of Cu and Hf become broadened after 5 h of milling. These diffraction peaks become negligible after ball milling for 40 h. It is significant to measure how the structures observed by the probe atoms change during mechanical alloying. Figure 2 shows the changes in the counting-rate ratio $R(t)$ during mechanical alloying. It is seen that the counting-rate ratio, after 15 min of milling, is identical with that of Hf metal, that is it becomes weak when the ball-milling time is increased and becomes negligible after ball milling for 40 h. One peak in the short-time region below 5 nsec, which is characteristic of the amorphous solids, grows after 40 h of milling. This implies that the electric-field gradient (EFG) around the Hf atoms may have a relatively broad distribution.[15,16] When the Bragg peaks of Hf metal have disappeared after 40 h of milling, the wave characteristic of Hf metal certainly disappeared in $R(t)$. This appears to be a little strange because it has been deduced that we can see microclusters or lamella layers of Hf by means of the microscopic method such as TDPAC. In particular, Johnson[17] has proposed the amorphization model by MA in which the nucleation of amorphous phases occurs at the diffused region near the interface of the lamella structure, which is rich in defects such as vacancies and dislocations. The present result might suggest that because the small lamellas of Hf layers are distributed due to defects, Hf sites in those layers do not show the counting-rate ratio $R(t)$ characteristic of hcp Hf metal. Recently Oguchi *et al.*[18] have performed the TDPAC measurements of multilayers of Hf and Cu, and observed that Hf

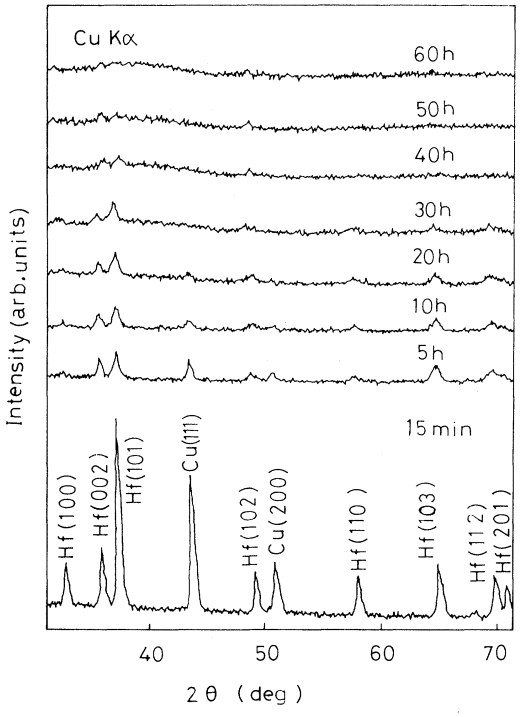


FIG. 1. X-ray-diffraction patterns of $Cu_{57}Hf_{43}$ alloys produced by mechanical alloying as a function of milling time.

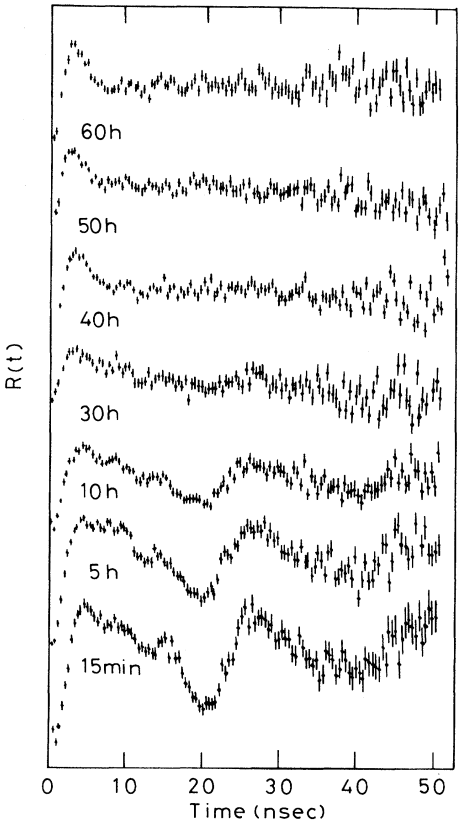


FIG. 2. The counting-rate ratio $R(t)$ of $Cu_{57}Hf_{43}$ alloys produced by mechanical alloying as a function of milling time.

sites in Hf layers whose thickness is below ~1000 Å, are much disturbed due to defects. As a result, the $R(t)$ of those Hf sites is not identical with that of hcp Hf metal. This result supports the previous suggestion. For comparison, we have done the TDPAC measurements of the melt-spun amorphous $Cu_{57}Hf_{43}$. Figure 3 shows the change in the counting-rate ratio $R(t)$ of the melt-spun $Cu_{57}Hf_{43}$ through isochronal annealing for 20 min. Certainly, there exist some waves in $R(t)$ of melt-spun amorphous $Cu_{57}Hf_{43}$. This reveals relatively clear structures around the Hf probe, which give a narrow distribution of the electric-field gradient. In addition, there is one peak in the short-time region below 5 nsec in $R(t)$ of as-spun amorphous $Cu_{57}Hf_{43}$. This indicates that the electric-field gradient around the Hf probe has a relatively broad distribution. It is suggested from the counting-rate ratio $R(t)$ that the as-spun amorphous $Cu_{57}Hf_{43}$ has short-range ordered- and disordered-Hf sites. The present result is different from that of amorphous Ga films prepared by evaporation at low temperatures.[19] It should be noted that the amorphous solid of a single component is special in many amorphous materials and is unstable in comparison with amorphous solids containing several components. In fact, the amorphous Ga film is unstable above ~17 K. On the other hand, the melt-spun amorphous $Cu_{57}Hf_{43}$ is stable until ~670 K. The thermal stabilities of these two amorphous solids are very different. In addition, because the as-spun specimen is melt spun through the temperature region in which intermetallic compounds are preferable, it is deduced that the melt-spun amorphous alloys tend to exhibit intermetallic compound-like short-range order. As shown in Fig. 3, the counting-rate ratio $R(t)$ does not change until annealing at 400 °C. After annealing at 500 °C, the $R(t)$ spectrum changes remarkably. This corresponds to a phase transition to the crystalline phase. The fits to the data are performed, taking into account the Gaussian-type spread of the resonant frequency; that is, we have analyzed the data by using

$$G_2(t)=S_{20}+\sum_{i=1}^{3} S_{2n}\cos(\omega_i t)\exp[-(\delta_i t)^2/2] .$$

Although it is now known whether the Gaussian-type spread is adequate, we adopt this approximation for qualitative discussions. Figures 4(a) and 4(b) show the $R(t)$ spectra of the amorphous $Cu_{57}Hf_{43}$ after ball milling for 60 h, and of the melt-spun amorphous $Cu_{57}Hf_{43}$, respectively. The solid lines are fitted ones. The counting-rate ratio $R(t)$ of the amorphous $Cu_{57}Hf_{43}$, which is prepared by mechanical alloying, is fitted well by the frequency ~950 Mrad/s with the broad spread $\delta_1$ ~340 Mrad/s. This means that the electric-field gradient around the Hf probe has a relatively broad distribution. Although a small discrepancy exists between the experimental data and the fitted line in the long-time region above ~15 nsec, the $R(t)$ of the melt-spun amorphous $Cu_{57}Hf_{43}$ is fitted by the frequency $\omega_1$~700 Mrad/s with the spread $\delta_1$~100 Mrad/s, the frequency $\omega_2$~1200 Mrad/s with the spread $\delta_2$~150 Mrad/s, and a broad peak with the frequency, which corresponds to that in the amorphous $Cu_{57}Hf_{43}$ prepared by mechanical alloying. Thus it is deduced that the short-range structures in the melt-spun amorphous $Cu_{57}Hf_{43}$ are composed of disordered short-range order and in addition, a relatively unique short-range order. Furthermore, the resonant frequencies of this unique short-range structure are similar to those of the $Cu_3Hf_2$ intermetallic compound.[20] That is, this implies that the melt-spun amorphous $Cu_{57}Hf_{43}$ may exhibit disordered short-range order and the intermetallic compoundlike $Cu_3Hf_2$ short-range order. It is of interest that the short-range structure around the Hf probe is much suppressed in the amorphous $Cu_{57}Hf_{43}$ prepared by mechanical alloying, compared with that in the melt-spun amorphous $Cu_{57}Hf_{43}$. Defects and stresses, which are introduced mechanically, might strongly disturb the

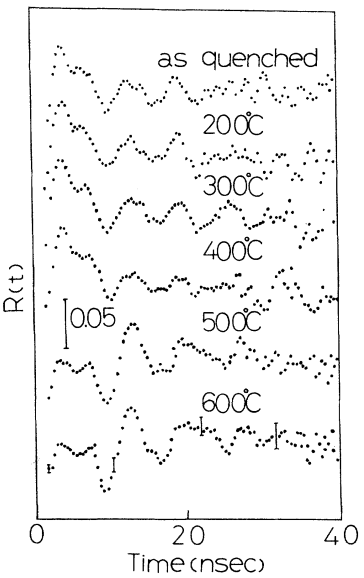


FIG. 3. The change in the counting-rate ratio $R(t)$ of the specimen $Cu_{57}Hf_{43}$ prepared by melt spinning during the isochronal annealing for 20 min intervals at temperatures 100 °C apart.

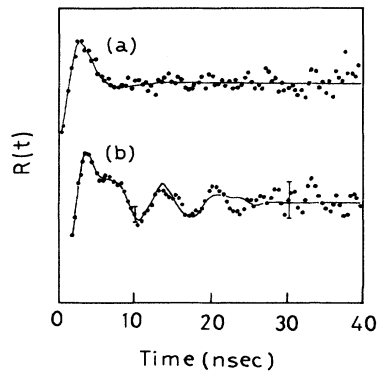


FIG. 4. (a) The counting-rate ratio $R(t)$ in the amorphous $Cu_{57}Hf_{43}$ after ball milling for 60 h. The solid line is the fitted one. (b) The counting-rate ratio $R(t)$ in the melt-spun amorphous $Cu_{57}Hf_{43}$. The solid line is the fitted one.

short-range structures. Recently it has been proposed that networks of disclinations are ordered, disordered, and hierarchical in the Frank-Kasper phase,[21] the amorphous phase, and the quasicrystalline phase,[22] respectively.[23,24] It is suggested that the broadly distributed sites in Figs. 4(a) and 4(b) might be assigned to the Hf sites in the dense disordered disclinations.

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