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Study on structural change of thermally-aged AlCu binary alloys by EXAFS

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1 Introduction

There are a lot of methods to control the properties of alloys. The thermal treatment is the most popular method especially in Al-alloys. It is because the thermal treatment can handle many specimens all at once and the process is not so difficult. On the other hand, irradiations with energetic charged-particles such as ions and electrons can also modify the properties of alloys. Irradiation has the advantages of controlling specific areas and depths of the modification. In addition, as the irradiation gives high energy into specimens, it can induce several changes which cannot be realized by conventional thermal treatments. Our previous studies indicate that by the ion irradiation, the Vickers hardness increases faster and the precipitates are much smaller than those induced by thermal treatments. We are going to reveal the mechanism of these irradiation-induced changes by measuring the extended X-ray absorption fine structure (EXAFS). However, as a first step, we measured the EXAFS spectra for specimens aged at elevated temperatures. A lot of researches have already studied aged Al-alloys such as the observation by transmission electron microscopy (TEM) [1] and the effect of Guinier-Preston (GP) zone as the cause of hardening by thermal treatment has been discussed. To the authors' knowledge, however, EXAFS measurements for thermally aged Al alloys have little been performed so far. Thus, in this report, we discuss the EXAFS results for aged AlCu binary alloys. The EXAFS is a useful tool for the observation of local atomic arrangements around selected atoms. Furthermore, this measurement is nondestructive testing, which is different from TEM observations. Therefore, it can evaluate the microstructures of specimens without observing any changes by specimen machining. We also performed FEFF simulations, and compared the simulation result with the experimental result. In order to reveal the relationship between the change in hardness and EXAFS spectra, Vickers hardness was also measured.

2 Experiment

Al-2wt%Cu and Al-4wt%Cu alloys were prepared by using 99.99 wt. % Al and 99.99 wt. % Cu. The two kinds of metals were mixed in a crucible above the melting temperature. In order to obtain supersaturated specimens, the resulting ingot of Al-Cu binary alloys were thermally annealed at 833 K for 48 h under atmosphere and then quenched into iced water. After this thermal treatment, the ingot was rolled into the sheet about 1 mm thick at room temperature. The sheet was cut into several specimens and solution treated at 833 K for aging and the EXAFS measurement. The surfaces of sheets were polished with #400, 600, 1200 and 2000 emery-papers. Finally, they were polished by using #3000 Al_2O_3 buff. Specimens of Al-2wt%Cu were aged at 453 K for 3 h and 6 h. Specimens of Al-4wt%Cu were aged at 453 K for 3 h, 6 h, 12 h and 1 day. These binary alloys were both quenched into iced water after the aging.

In order to observe the local structures around Cu atoms in the lattice structure of the solution-treated specimens and the aged specimens, we performed the EXAFS measurements around the Cu K absorption edge (8.33 keV) at the 27B beamline of the synchrotron radiation facility of High Energy Accelerator Research Organization (KEK-PF). The EXAFS spectra were obtained by using the fluorescence method with a 7 element germanium x-ray detector at room temperature. As a reference data, the EXAFS spectrum for a pure Cu 5μm thick was obtained by the transmission method. We used the computer software, WinXas [2], for analyzing the obtained EXAFS spectra. In the analyses, all EXAFS spectra were Fourier transformed using k^3 weighting with the k range from 2 - 3 to 10 - 15 $Å^{-1}$. Besides, EXAFS simulations were performed using the computer code, FEFF [3]. In this study, to simulate the state of Cu precipitates, FEFF simulations were performed for the following atomic arrangements; (1) a Cu atom which replaces an Al atom exist in Al matrix, (2) all the nearest neighbor atoms for a Cu atom replacing Al atom are Cu atoms, (3) all the nearest neighbor and 2^{nd} nearest neighbor atoms for a Cu atom replacing Al atom are Cu atoms, (4) all the nearest neighbor, 2^{nd} nearest neighbor and 3^{rd} nearest neighbor atoms for a Cu atom replacing Al atom are Cu atoms.

The surface hardness change was estimated by using a Vickers hardness tester at room temperature with a load of 98.07mN (10 gf). The time interval of indentation was kept at 10 seconds. The hardness values were obtained by averaging the values from 10 indentations.

3 Results and Discussion

Fig. 1 shows the Fourier transformed (FT) EXAFS spectra near Cu K absorption edge for the Al-2wt%Cu specimens which were thermally aged at 453 K. For comparison, the spectra for the solution treated specimen and the pure Cu are also shown. The peak intensity of 3 h aged specimen dramatically decreases when compared with that of solution treated specimen. However, the peak intensity of 6 h aged specimen shows a little increase from that of 3 h aged specimen. Fig. 2 shows the change in Vickers hardness for the thermally aged Al-2wt%Cu as a function of aging time. As is well known, the hardness gradually increases as the aging time increases and it decreases after aging time of more than 3 days. Considering Fig. 1 and Fig. 2, EXAFS measurement detects very small precipitates, which were produced by the short time aging, as the change in spectrum intensity.

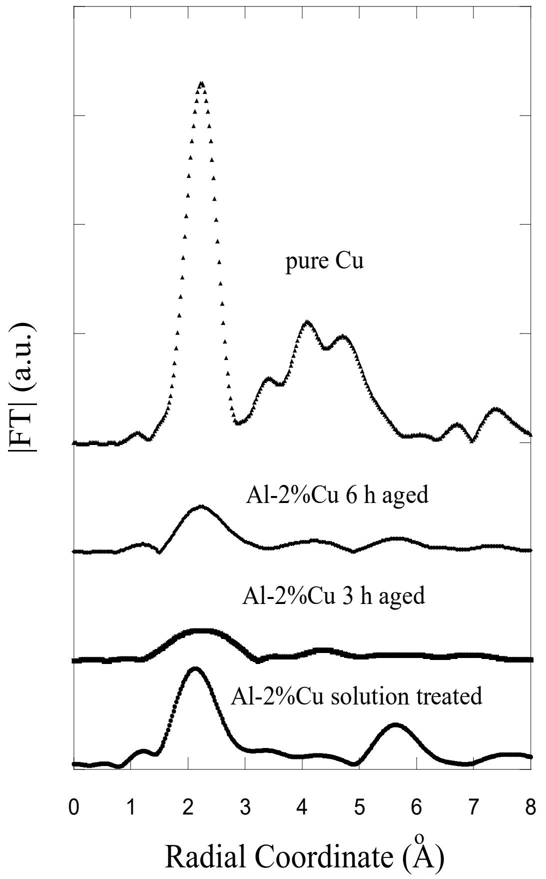

Fig. 1 FT EXAFS spectra near Cu K absorption edge for Al-2wt%Cu thermally aged at 453 K, Spectra for solution treated specimen and pure Cu are also shown.

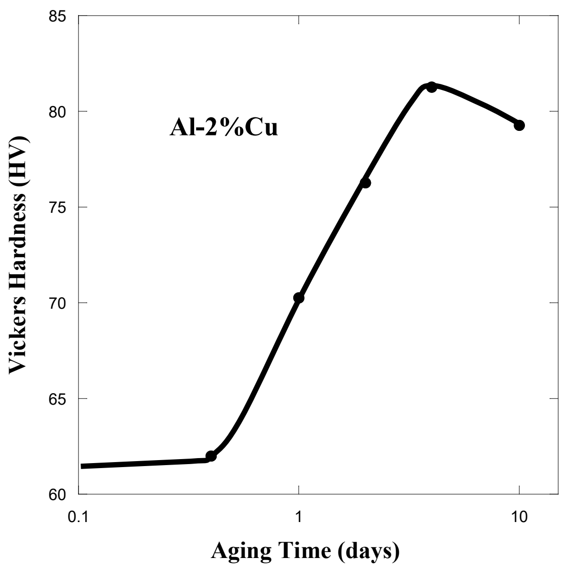

Fig. 2 Change in Vickers hardness for the Al-2wt%Cu as a function of aging time. Aging temperature is 453K.

The effect of thermal aging on the EXAFS spectrum can be observed more clearly for Al-4wt% Cu specimens. Fig. 3 shows the FT EXAFS spectra near Cu K absorption edge for the Al-4wt% Cu specimens thermally aged at 453 K. For comparison, the spectra for the solution treated specimen and the pure Cu are also shown. The peak intensity largely decreases for the short aging time. As the aging time increases, the peak intensity gradually increases. The intensity of 1st nearest peak for the 1 day aged specimen is the same as that for the solution treated specimen and the intensity becomes much larger while aging time is longer than 1 day.

In addition, the shape of the spectra becomes similar to that of pure Cu. Fig. 4 shows the change in Vickers hardness for the thermally aged Al-4wt%Cu specimens as a function of aging time. The hardness gradually increases as the aging time increases and it decreases after the aging of more than 1 day. Therefore, considering Fig. 3 and Fig. 4, peak intensities are small when Cu precipitates induced by the thermal aging are too small to harden the specimens. On the other hand, when precipitates are large enough to harden the specimens, the peak intensities gradually increases and they become larger than that for the solution treated one.

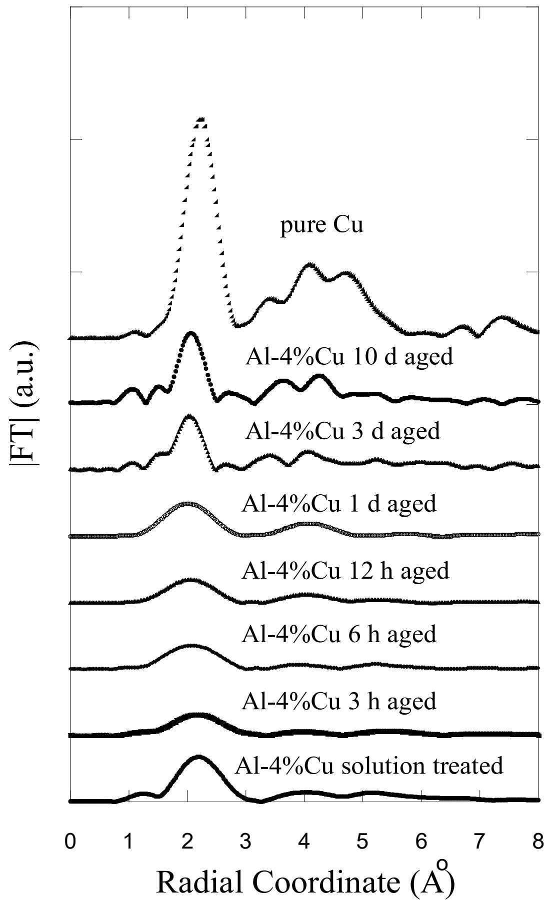

Fig. 3 FT EXAFS spectra near Cu K absorption edge for Al-4wt%Cu thermally aged at 453 K, Spectra for solution treated specimen and pure Cu are also shown.

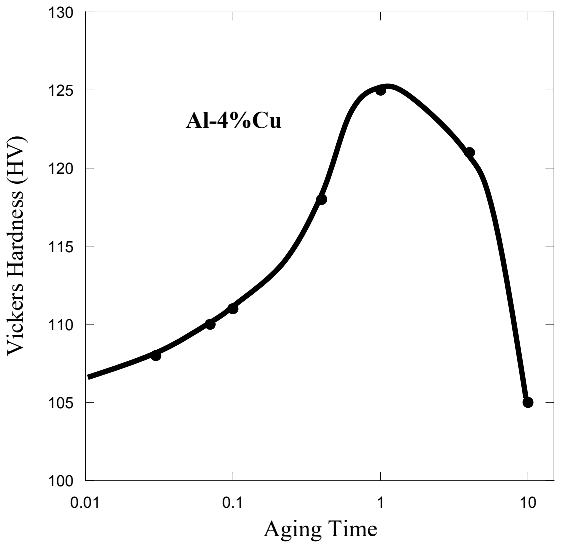

Fig. 4 Change in Vickers hardness for the Al-4wt%Cu as a function of aging time. Aging temperature is 453K.

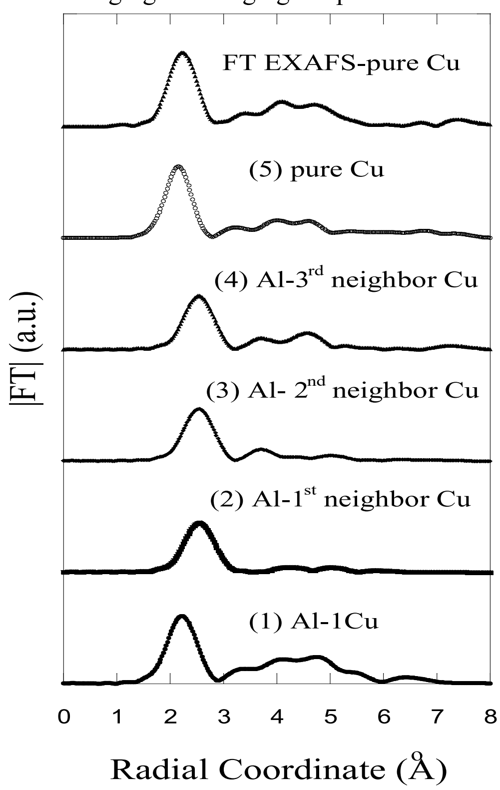

Fig. 5 Simulated spectra by using FEFF code for the following atomic arrangements; (1) a Cu atom which replaces an Al atom exist in Al matrix, (2) all the nearest neighbor atoms for a Cu atom replacing Al atom are Cu atoms, (3) all the nearest neighbor and 2nd nearest neighbor atoms for a Cu atom replacing Al atom are Cu atoms, (4) all the nearest neighbor, 2nd nearest neighbor and 3rd nearest neighbor atoms for a Cu atom replacing Al atom are Cu atoms, (5) pure Cu. Experimental spectrum for pure Cu is also shown for comparison.

Fig. 5 shows the simulated spectra by using FEFF code for the following atomic arrangements; (1) only one Cu in fcc Al, (2) 1st nearest neighbor atoms are Cu, (3) 1-2nd nearest neighbor atoms are Cu, (4) 1-3rd nearest neighbor atoms are Cu, and (5) pure Cu. To compare with the simulated results, The experimental FT EXAFS spectrum for pure Cu is also shown. First of all, the result of simulated spectrum for pure Cu is quite similar to the experimental spectrum for pure Cu. Therefore, the present simulations are reliable enough to discuss the changes in EXAFS spectra by the thermal aging. The peak intensity once decreases when only a few Cu aggregates, and it turns to increase as the Cu precipitates become larger. These changes are observed by both experiments and simulations. Therefore, it is confirmed that change in EXAFS spectra truly observes the change in the structure of Cu atoms in Al matrix by the thermal aging.

The present experimental result shows that not only huge precipitates but also very small precipitates produced by the short time thermal aging can be detected by using the EXAFS measurement.

<u>References</u>

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