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XAFS analysis of Cu-Ti alloys after thermal and chemical treatment

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Introduction

Amorphous alloys have a non-equilibrium state and crystallize by heating. The thermal treatment at appropriate temperature brings about a structural rearrangement of amorphous alloy, which leads to structural transformation of amorphous alloy into various intermediate states. The alloys in intermediate crystalline states have potential to show specific properties different from those of amorphous and crystalline alloys.

The amorphous alloy prepared by rapid quenching method has quite low surface area. Preparation of skeletal catalyst by extracting a component selectively from multi-component alloys by chemical treatment has been applied to obtain metal catalysts with high surface area. In this study, the relationship between the catalytic performance of skeletal Cu and the structural transformation of Cu-Ti amorphous alloy caused by thermal treatment was investigated. Skeletal Cu catalysts were prepared from Cu-Ti alloys via heating at various temperatures and following HF treatment for extraction of Ti.

Experimental

An amorphous CuTi (denoted as amor-CuTi) alloy in the shape of ribbon was prepared from crystalline mother alloy by the rapid quenching method. The heat treatments of amor-CuTi were carried out in a temperature range from 473 to 873 K under vacuum for 2 h. These heated samples were denoted as CuTi(t) (t=473-873 K). For extraction of Ti moieties, amor-CuTi and heated CuTi(t) were treated with aqueous HF solution, and then thoroughly washed with ion-exchanged water. The catalytic performances of samples were tested by hydrogenation of *p*-NP to *p*-AP as a model reaction.

XAFS spectra at Cu K-edge were measured in the transmission mode at 298 K. Obtained data were examined using the analysis program (Rigaku REX2000).

Results and Discussion

The crystallinity of amor-CuTi and CuTi(t) was investigated by XRD measurements. The amor-CuTi and heated CuTi below 573 K only showed a similar broad peak (halo). After heating at 673 K, three sharp diffraction peaks were observed, showing the existence of CuTi crystalline phase. These XRD patterns exhibited that amor-CuTi began to crystallize between 573 K and 673 K.

The local structure of amor-CuTi, CuTi(573) and CuTi(873) was investigated by XAFS measurements. As shown in Figure 1, Fourier transform of EXAFS spectra of amor-CuTi, CuTi(573) and CuTi(873) exhibited a peak attributed to the contiguous Cu-Cu bond. The peak intensity of CuTi(873) was higher than that of amor-CuTi and CuTi(573). XRD investigations showed that CuTi(873) had crystalline phase. The increase of peak intensity of CuTi(873) was caused by crystallization of amor-CuTi. Figure 1 also showed the peak shift of CuTi(873) (at ca. 2.2 Å) to longer atomic distance than that of amor-CuTi and CuTi(573) (at ca. 2.1 Å). In amorphous phase, Cu and Ti atoms were packed more densely than that of crystal, since the atomic arrangement of amorphous alloy is similar to that of liquid. The atomic arrangement of amorphous alloy was considerably differ from that of crystalline alloy in the structural order.

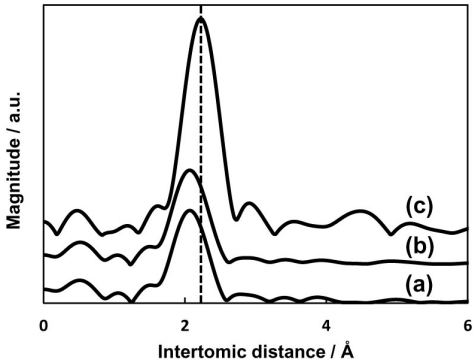

Figure 1 Fourier transforms of EXAFS spectra of (a) amor-CuTi, (b) CuTi(573) and (c) CuTi(873).

The SEM images and EDX data clearly showed the formation of porous structure and successful extraction of Ti moieties through the HF treatment of untreated and heated samples.

The catalytic performances of skeletal Cu catalysts prepared from heated amor-CuTi at various temperatures were tested by hydrogenation reaction of *p*-NP to *p*-AP. The catalytic activities of skeletal Cu catalysts increased with increasing heating temperature and maximized at 573 K. This might be caused by structural transformation of amor-CuTi. The thermal treatment at 573 K was effective leading to atomic migration in the amorphous alloy. This atomic migration causes the difference in the catalytic activity. At higher temperatures above 573 K, a decrease in the catalytic activity was observed. This change might occur due to the crystallization and the grain growth. The thermal treatment at lower than crystallization temperature of amor-CuTi strongly enhances the catalytic activity of skeletal Cu catalyst.

References

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