

## 질소가스 분위기 중 기계적 합금화에 의한 Cu-V 및 Fe-Cr계의 비정질화 과정

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Amorphization Process Induced by Mechanical Alloying under N<sub>2</sub> Gas  
Atmosphere in Cu-V and Fe-Cr System.

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초 록 질소가스 분위기 중에서 Cu<sub>30</sub>V<sub>70</sub> 및 Fe<sub>30</sub>Cr<sub>70</sub> 혼합분말을 기계적 합금화(MA) 처리한 결과, 두 합금계에서 비정질화가 관찰되었다. 결정질에서 비정질상으로의 구조변화 과정을 X선 회절 및 중성자 회절법에 의해 관찰하였다. 그 결과, 이 합금계에서의 비정질화는 각 결정구조에서 전형적으로 존재하는 8면체 unit가 선택적으로 붕괴되어 4면체 unit로 변화되어 가는 과정임을 알 수 있었다. 또한, 중성자회절 결과로부터 질소원자는 금속원자로 이루어진 4면체의 중심에 위치하고 있음을 알 수 있었다.

**Abstract** Mechanical alloying(MA) of Cu<sub>30</sub>V<sub>70</sub> and Fe<sub>30</sub>Cr<sub>70</sub> powders was carried out under the N<sub>2</sub> gas atmosphere. Amorphization has been observed in these two cases, while MA under an inert gas atmosphere produces the bcc solid solution. Structural transformation from the crystalline to amorphous states was observed through X-ray and neutron diffractions. During amorphization process the octahedral unit, which is typical of a polyhedron formed in any crystal structures, was preferentially destroyed and transformed into the tetrahedral unit. Moreover, neutron diffraction measurements revealed that a nitrogen atom is situated at a center of the tetrahedron formed by metal atoms.

### 1. INTRODUCTION

Mechanical alloying has attracted much attention as a novel technique to synthesize non-equilibrium phases through the solid state reaction under intense mechanical deformations<sup>1-3)</sup>. MA has been usually carried out under an inert gas atmosphere in order to protect sample powders from oxidation, since a fresh cleavage surface created during milling is of vital importance in the solid state reaction. Recently, however, MA under a controlled gas atmosphere has been reported to

produce a non-equilibrium phase through the solid-gas reaction<sup>4-7)</sup>. In this study, I focus on the structural changes during the amorphization process induced by nitrogen atoms.

### 2. EXPERIMENTAL

Pure elemental powders of copper(99%, average size 150 $\mu$ m), vanadium(99.5%, average size 50 $\mu$ m), iron(99%, average size 75 $\mu$ m) and chromium(99.9%, average size 75 $\mu$ m) were mixed to give starting compositions of Cu<sub>30</sub>V<sub>70</sub> and Fe<sub>30</sub>Cr<sub>70</sub>. MA for Fe<sub>30</sub>Cr<sub>70</sub> powders was carried out in a vibrating ball mill(Nissin

Gikken, Super MISUNI) and for  $\text{Cu}_{30}\text{V}_{70}$  powders in a planetary ball mill(Fritsch Pulverisette 5) under the  $\text{N}_2$  gas atmosphere of 2 atmospheric pressure. During milling,  $\text{N}_2$  gas was supplied to resume 2 atmospheric pressure at every twenty hours. Amorphization was confirmed by the DSC measurement and X-ray diffraction with Cu-K radiation. The total contents of nitrogen atoms absorbed in the powders was determined, using the nitrogen-oxygen analyzer(Horiba EMGA-650). A detailed structural study was carried out by using the combination of X-ray diffraction with Mo-K $\alpha$  radiation and neutron diffractions.

The neutron diffraction spectra were measured, using High Intensity Total(HIT) scattering spectrometer at High Energy Physics Laboratory, Tsukuba, Japan. Spallation pulsed neutrons produced by proton accelerators are useful for characterizing the highly resolved structure of atomic scale length in amorphous alloy. Experimental details and data analyses of neutron diffraction spectra have been described in previous works<sup>8,9</sup>.

The X-ray diffraction measurement revealed that the metal atoms change their respective positions during the amorphization process. But the presence of nitrogen atoms is hardly visible in the spectrum because of its negligibly small scattering factor. Instead, neutron diffraction allows us to observe atomic rearrangements around a nitrogen atom since the coherent scattering length of a nitrogen atom is almost the same as or even larger than those of the metal atoms.

### 3. RESULTS AND DISCUSSION

#### Cu-V-N system

Cu and V atoms are mutually immiscible even in the liquid state and its system is characterized by a positive heat of mixing  $\Delta H_{\text{mix}} = 5$  kJ/mol. The MA of  $\text{Cu}_{30}\text{V}_{70}$  powders in the Ar gas atmosphere has been reported to produce the bcc solid solution<sup>10</sup>.

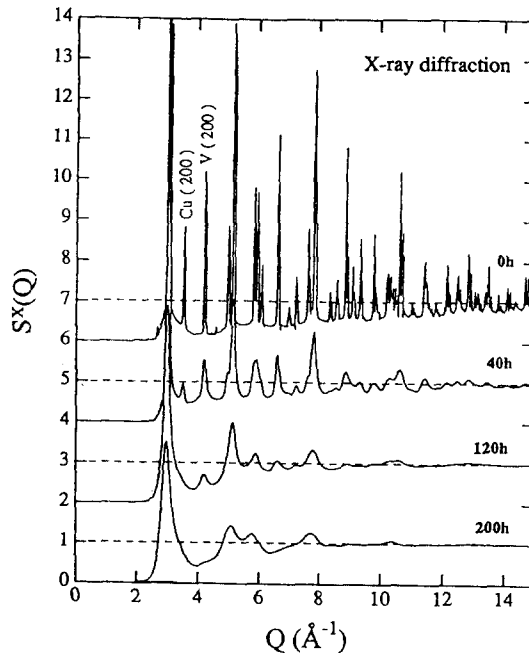


Fig. 1. X-ray structure factors  $S^X(Q)$  of  $(\text{Cu}_{30}\text{V}_{70})_{1-x}\text{N}_x$  powders after 0, 40, 120 and 200 hours of MA.

Figure 1 shows the  $S^X(Q)$  observed by X-ray diffraction after 0, 40, 120 and 200 hours of milling. The content of nitrogen atoms absorbed was determined as 0, 3.4, 9.2 and 11.7 at%N, respectively. After 200 hours of milling, the  $S^X(Q)$  shows a characteristic feature of an amorphous state, though some small Bragg peaks remain due to small amount residual unreacted crystals. Especially, the peaks due to (200) planes of the fcc-Cu and bcc-V structures decrease and disappear.

Figure 2 shows  $\text{RDF}^X(r)$  derived from the Fourier transformation of the corresponding  $S^X(Q)$ . The  $\text{RDF}^X(r)$  before MA clearly reflects the atomic distributions of fcc-Cu and bcc-V crystals. The first peak at 2.61 Å corresponds to the nearest neighbors of the Cu-Cu correlation in the fcc structure and the V-V correlation in the bcc structure. The second and third peaks at 3.09 and 3.62 Å are identified as the second nearest neighbors of the V crystal and the second one of the Cu crystal, respectively. It is clear that the  $\text{RDF}^X(r)$  gradually changes into the structure characteristic of an amor

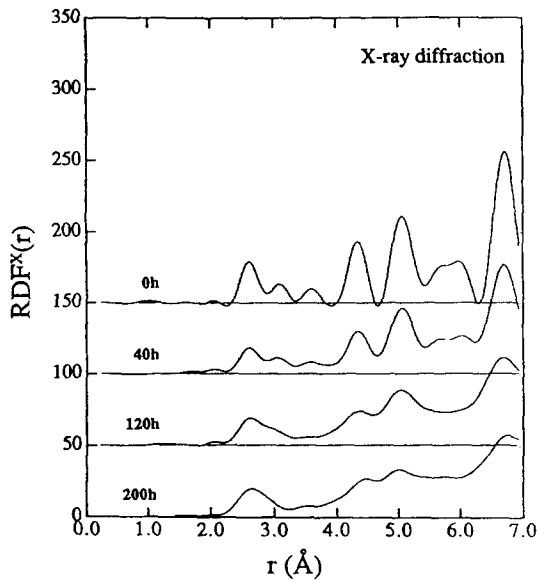


Fig. 2. X-ray radial distribution functions  $RDF^X(r)$  for  $(Cu_{30}V_{70})_{1-x}N_x$  powders after 0, 40, 120 and 200 hours of MA.

-phous state with increasing milling time. Especially, the atoms at the second nearest location of 3.09 Å for the bcc-V crystal and of 3.62 Å for the fcc-Cu crystal change their positions during milling.

The disappearance of the peak associated with the (200) plane in the fcc and bcc crystal structure have been already observed during the amorphization process subjected to MA in the Ni-V<sup>(11)</sup> and Cu-Ta<sup>(12)</sup> systems. This is consistent with the conclusion that the octahedral units found in an fcc and bcc crystals are preferentially destroyed during amorphization.

The  $S^N(Q)$  observed by neutron diffraction is shown in Fig. 3. The spectrum after 200 hours of milling possesses a mixture of both amorphous and crystal states. Since the coherent scattering length of the V atom in the neutron diffraction is negligibly small, small crystal peaks should be due to the Cu crystal. More detailed inspection of  $S^N(Q)$  allows us to identify the growth of a new peak at  $Q \sim 4.25 \text{ \AA}^{-1}$  after 40 and 120 hours of milling, which disappears after 200 hours of milling. This peak is attributable to the bcc-Cu crystal formed by

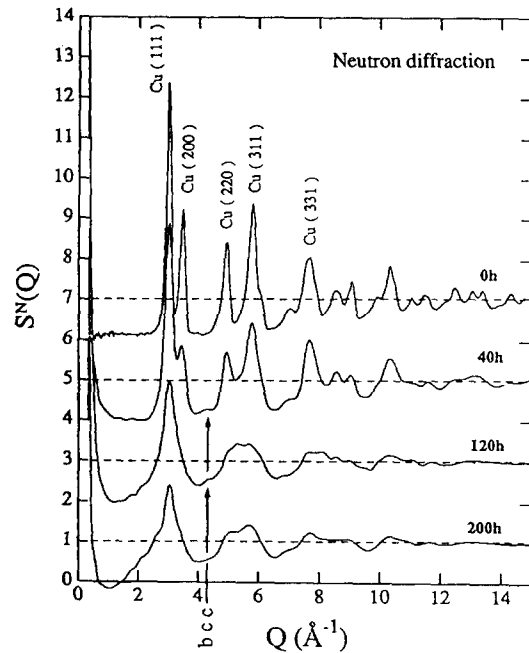


Fig. 3. Neutron structure factors  $S^N(Q)$  of  $(Cu_{30}V_{70})_{1-x}N_x$  powders after 0, 40, 120 and 200 hours of MA.

dissolving Cu atoms into the bcc-V lattice<sup>(10)</sup>. Therefore, we consider that the bcc solid solution is formed at the early stage of milling but it becomes amorphized due to the gradual incorporation of nitrogen atoms in the subsequent stage of milling. The Cu atoms first dissolve into the V lattice and apparently prevent V atoms from the formation of nitrides. Indeed, we confirm that the MA of pure V powders in the  $N_2$  gas atmosphere results in only VN crystalline compound.

#### Fe-Cr-N system

The Fe-Cr system has a small negative heat of mixing  $\Delta H_{mix} = -1 \text{ kJ/mol}$  and is characterized by the complete solid solution over an entire composition range. The MA of this powders under Ar gas atmosphere has been reported to only yield the bcc solid solution. In contrast, the  $Fe_{30}Cr_{70}$  powders were amorphized by MA in  $N_2$  gas atmosphere<sup>(10)</sup>.

Figure 4 shows the X-ray structure factor  $S(Q)$  for  $(Fe_{30}Cr_{70})_{1-x}N_x$  powders subjected to the MA process for different time intervals. It is seen that Bragg peaks of the bcc Fe and

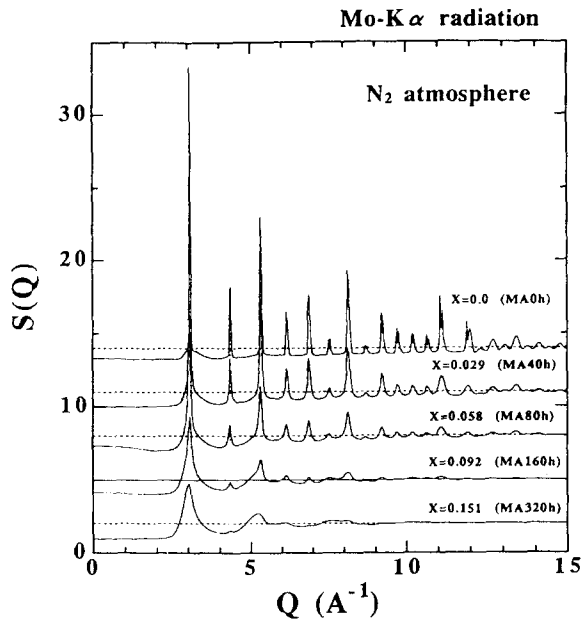


Fig. 4. X-ray structure factors  $S(Q)$  of  $(Fe_{30}Cr_{70})_{1-x}N_x$  powders after 0, 40, 80, 160 and 320 hours of MA.

Cr crystals become broadened with increasing the milling time. A halo pattern dominates after 320 hours of MA. As shown in Fig. 4 the concentration of nitrogen atoms absorbed during MA increases with increasing the milling time and approaches about 15 at%N after 320 hours of milling. This results indicate that the nitrogen atom apparently contributes to destroy the bcc structure and to form an amorphous structure.

The radial distribution function  $RDF(r)$  derived from the Fourier transformation of  $S(Q)$  is shown in Fig. 5. The first peak at 2.44 Å corresponds to the nearest neighbors of the Fe-Fe and Cr-Cr correlation in the bcc structure. The second and third peaks at 2.95 and 3.43 Å are identified as the 2nd and 3rd nearest neighbors of the bcc crystal, respectively. As marked by an arrow, the 2nd nearest neighbor atoms in the bcc crystal preferentially reduce the number during the amorphization process. It is also seen that the 1st nearest neighbor distance between metal atoms expands with increasing the milling time. We found further that the nearest coordination

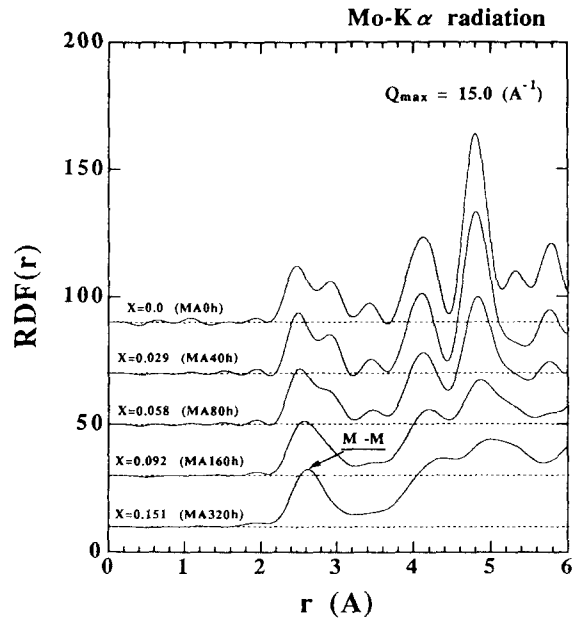


Fig. 5. X-ray radial distribution functions  $RDF(r)$  of  $(Fe_{30}Cr_{70})_{1-x}N_x$  powders after 0, 40, 80, 160 and 320 hours of MA.

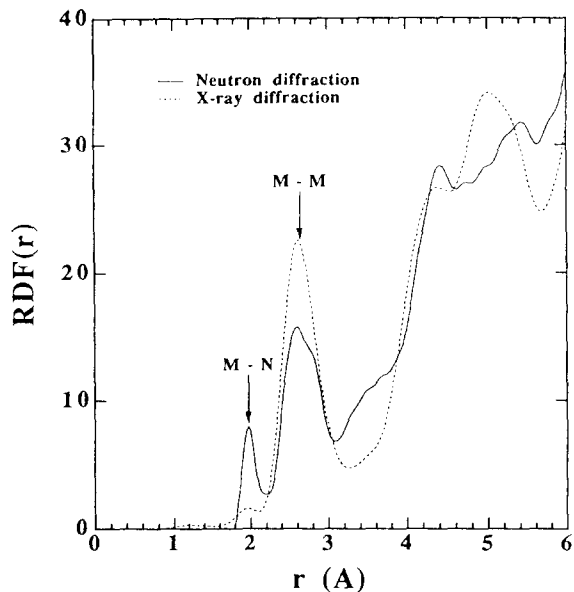


Fig. 6. Radial distribution functions  $RDF(r)$  of  $(Fe_{30}Cr_{70})_{0.83}N_{0.15}$  powders observed by X-ray and neutron diffractions.

number around a metal atom within about 3.3 Å decreases from 14 to 11.9 atoms. We are, therefore, led to conclude that the octahedral unit in a bcc structure is preferentially de-

stroyed and is transformed into the tetrahedral unit during the amorphization process. An increase in metal-metal(M-M) distance of the 1st nearest neighbor with increasing milling time can be interpreted by assuming that nitrogen atoms are accommodated in the center of a polyhedron formed by metal atoms.

Neutron diffraction experiments can provide further detailed information about the local structure surrounding the nitrogen atom. Figure 6 compares RDF(r) of  $(\text{Fe}_{30}\text{Cr}_{70})_{0.85}\text{N}_{0.15}$  powders deduced from both X-ray and neutron diffractions. The peak at about 2 Å observed only in the neutron diffraction spectra can be safely ascribed to the metal-nitrogen (M-N) atom correlation. The coordination number of metal atoms around a nitrogen atom turns out to be 4. This implies that the nitrogen atom is located at a center of the tetrahedron formed by metal atoms.

#### 4. SUMMARY

The MA under the  $\text{N}_2$  gas atmosphere is capable of amorphizing both the  $\text{Fe}_{30}\text{Cr}_{70}$  and  $\text{Cu}_{30}\text{V}_{70}$  powders, the former being characterized by a small negative heat of mixing ( $\Delta H_{\text{mix}} = -1\text{kJ/mol}$ ) and the latter by a positive heat of mixing ( $\Delta H_{\text{mix}} = 5\text{kJ/mol}$ ). The amorphization is brought about only in the presence of nitrogen atoms; since both powders become bcc solid solutions by MA under the Ar gas atmosphere. Therefore, the nitrogen atom preferentially destroys the octahedral unit in the bcc structure and contributes to form an amorphous structure, which is known as being mainly composed of tetrahedral units, through the solid-gas reaction occurring during the MA process.

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