기계적 합금화법으로 제조한 비정질 Ni-Ta 및 Cu-Ta 합금분말의 중성자회절에 관한 연구

A Study on Neutron Diffraction of Amorphous Ni-Ta and Cu-Ta Alloy Powders Prepared by Mechanical Alloying.

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요 약

기계적 합금화법에 의한 비정질화 과정을 Ni-Ta 계 및 Cu-Ta 계에 대하여 조사하였다. Ni-Ta합금계는 혼합엔탈피가 음이나, Cu-Ta계는 혼합엔탈피가 양인 열역학적으로 대조적인 합금계이다. 볼밀 중 발생하는 원자구조 변화를 중성자회절법을 이용하여 관찰하였다. 두 합금계에 있어서 기계적 합금화에 의한 비정질상이 생성되었다. 비정질 Cu-Ta합금의 local 원자구조를 혼합엔탈피가 크게 음인 Ni-Ta계의 결과와 비교하였다. 그 결과, 대조적 특성을 가진 두 합금계임에도 불구하고 원자크기가 작은 Ni 및 Cu 가 bcc Ta의 결정격자 속으로 우선적으로 침입함으로써 비정질화가 진행됨을 알 수 있었다.

Key Words(중요용어) : Neutron diffraction(중성자회절), Amorphous phase(비정질상), Atomic structure (원자 구조), Mechanical alloying(기계적합금화), Solid state reaction(고상반응)

1. Introduction

The solid state reaction by mechanical alloying generally proceeds by lowering the free energy as a result of chemical reaction at the interface between the two adjacent layers[1]. However, it has been also known that some thermodynamically stable intermetallic compounds can be made amorphous when subjected to mechanical alloying[2]. In this case, a phase transition should involve an increase in the free energy, and the accumulation of strains and defects has been believed to be responsible for it[3]. But its mechanism has not yet been well understood. A similar situation is also expected to occur in mechanical alloying process for a mixture of two different pure elements with a positive heat of mixing, since no chemical driving force to lower the free energy is a prior present in these systems.

Many binary systems consisting of Cu and transition metal elements like Fe and Mo are characterized by a positive heat of mixing[1]. For example, the Cu-Ta system forms essentially no solid solution over a whole concentration range[2]. In the present study, we report on the mechanical alloying process in the Ni-Ta and Cu-Ta as representatives of systems with a negative and positive heat of mixing, respectively. The formation process of an amorphous phase and its local atomic structure in the Cu-Ta system are directly compared with those obtained for the Ni-Ta system with a large negative heat of mixing. In this way, we can point out what is the uniqueness in the amorphization process induced by solid state reaction during mechanical alloying.

2. Experimental

The mechanical alloying was carried out at room temperature in an argon gas atmosphere, using pure Cu (99.9%, <150 μm in average size), Ni (99.9%, <150 μm in size) and Ta (99.9%, 50 μm in size) powders.

Pure metal powders were mixed so as to have following average atomic compositions: $Cu_{30}Ta_{70}$ and $Ni_{30}Ta_{70}$. A planetary-type ball mill (Fritsch Pulverisette 5) was used with its intensity of 5. The vial and balls made of Cu-Be (Be of 1.8-2.0 at.%) alloy were used for the Cu-Ta samples to avoid iron contamination. But the vial made of SKD11 was employed for the Ni-Ta samples. The total mass of powders was about 20 g and the ratio of balls to powders was about 7:1.

The thermal properties for samples by milling times have been studied by DSC (differential scanning calorimetry) in combination with ordinary X-ray diffraction with Cu-Kα radiation.

The nitrogen-oxygen analyzer (Horiba EMGA -650) was employed to determine the oxygen and nitrogen contaminations. It turned out that a mixture of Cu and Ta powders before milling has already contained O_2 of 1.3 at.% and N_2 of 0.3 at.%. The values increased only to O_2 of 1.7 at.% and N_2 of 0.5 at.% after 120 hour of milling. Hence, we ignore the effect of such impurities on the formation of metastable phases in Cu-Ta systems.

The neutron diffraction spectra were measured, using High Intensity Total (HIT) scattering spectrometer at High Energy Physics Laboratory, Tsukuba, Japan. From the total structure factor S(Q) in the Faber-Ziman expression[6] for the samples studied, we obtain for $Cu_{30}Ta_{70}$

$$S(Q)=0.1047S_{CuCu}(Q)+0.4378S_{CuTa}(Q)+0.4573S_{TaTa}(Q), \qquad (1)$$

and for $Ni_{30}Ta_{70}$

$$S(Q)=0.1522S_{NiNi}(Q)+0.4759S_{NiTa}(Q)+0.3719S_{TaTa}(Q) \qquad (2)$$

where $S_{ij}(Q)$ represents partial structure factor related to i-j atomic correlation.

3. Results and Discussion

From the Cu-Ta phase diagram[5], we may assume that a homogeneous liquid is formed but no solid solution exists over a whole concentration range. Thus, the heat of mixing is positive and evaluated to be +2 kJ/mol for the $Cu_{50}Ta_{50}$[1]. A main feature in the phase diagram changes dramatically when Cu is replaced by its neighboring element Ni. The existence of several intermetallic compounds in the Ni-Ta system[5] immediately implies the possession of a negative value of ΔHmix: for example, -29 kJ/mol for $Ni_{50}Ta_{50}$[1].

The X-ray diffraction spectra were taken as a function of milling time for Cu-Ta[8] and Ni-Ta. In Ni-Ta, both Ni and Ta diffraction lines equally decrease their intensities within a few h of milling and are gradually replaced by a halo characteristic of an amorphous phase. Instead, the diffraction lines of Cu in Cu-Ta disappear first while that of Ta remains essentially unchanged within 30 hour of milling. However, the Ta lines in the Cu-Ta system substantially broaden and approach a halo-like pattern when milling time reaches 50-100 hour, suggesting that an amorphous phase is slowly formed.

The DSC spectra for the $Cu_{30}Ta_{70}$ system exhibit a sharp exothermic peak at about 550°C after 100 hour of milling[8]. The X-ray diffraction analysis after the first DSC run revealed a complete decomposition into pure elements Cu and Ta without formation of any other compounds including oxides. The base line in the DSC spectra was determined by taking the second run after decomposition into pure elements for each sample. The area enclosed by the first and second runs represents a total enthalpy ΔHt accumulated during milling. The value of ΔHt tends to level off at the value of 12 kJ/mol in $Cu_{30}Ta_{70}$ system. This value was noted to agree with the free energy gain necessary to transform a mixture of pure metals Cu and Ta into an amorphous phase[7].

The S(Q) for the Cu-Ta system is shown in Fig.1. The Cu lines disappear first and the profile approaches that typical of an amorphous phase after 120 hour of milling. The S(Q) is also shown in Fig.2 for a series of the $Ni_{30}Ta_{70}$ powders by milling times. Diffraction peaks due to both Ni and Ta are almost equally broadened and weakened within 5 hour of milling and an amorphization apparently completes after 80 hour of milling. An almost simultaneous decay of diffraction lines of both early and late transition metal elements within a few hour of milling is a universal feature observed in systems with a negative heat of mixing[9]. The (200) diffraction peaks correspond to the second nearest neighbor atoms in both fcc Ni and bcc Ta. Fig.2 clearly shows that these peaks are weakened much faster than those associated with the first and third nearest neighbors. The second nearest neighboring atoms are known to form the apex in octahedral units in both fcc and bcc. A selective decay of the (200) diffraction lines implies the preferential destruction of octahedral units in an fcc and bcc structure. Therefore, the amorphization steadily proceeds from the beginning of milling in a system with a negative heat of mixing by the preferential destruction of octahedral units, which, in turn, results in an increase in a fraction of tetrahedral units[9]. In contrast, the diffraction lines associated with pure Cu disappeared first in Cu-Ta system. Next, we discuss the local atomic structure derived at the final stage, where an amorphous phase is formed in both Cu-Ta and Ni-Ta systems.

A local atomic environment around Cu and Ta atoms can be studied quantitatively by analyzing the first peak in the total pair distribution function g(r) after the completion of amorphization. The results for the Cu-Ta system are shown in Fig.3. The data before milling is shown as a reference. The double-peaked spectrum can be decomposed into Cu-Cu and Ta-Ta pairs, as shown in Fig.3(a). As listed in Table 1, the coordination number of the Cu-Cu and Ta-Ta pairs in the starting sample agrees well with that of 12 and 8 inherent to
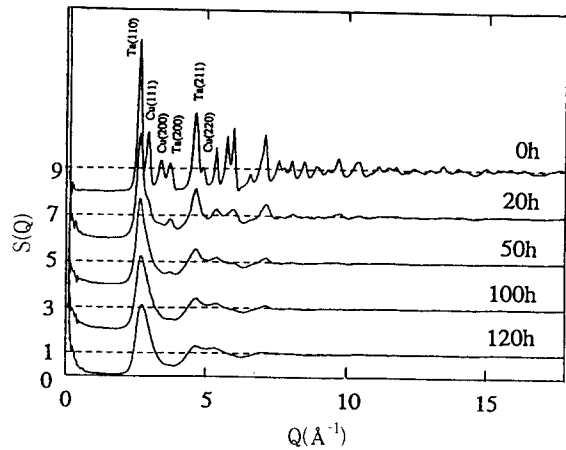

Fig.1. Total structure factor S(Q) of the Cu: Ta=3:7 powders by milling times.
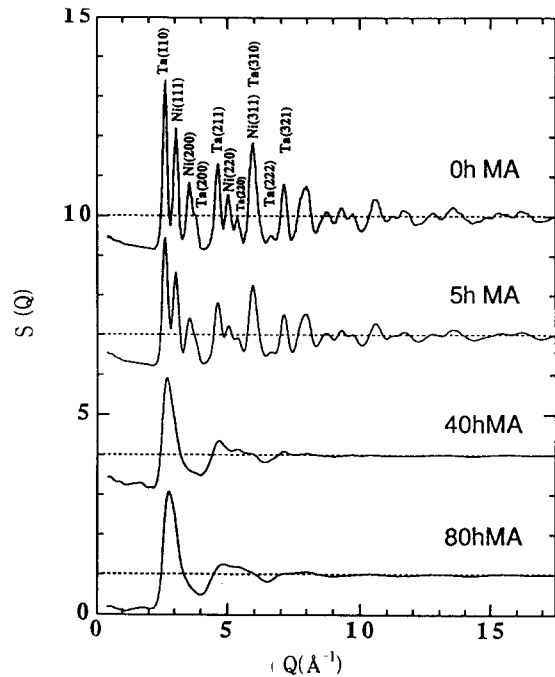

Fig.2. Total structure factor S(Q) of the Ni: Ta=3:7 powders by milling times.

the fcc and bcc structures, respectively. An asymmetric singled peak is formed after amorphization. Obviously, this is due to the emergence of the Cu-Ta correlation. The total pair distribution function is now decomposed into Cu-Cu, Ta-Ta and Cu-Ta pairs, as shown in Fig.3(b). The numerical results obtained by
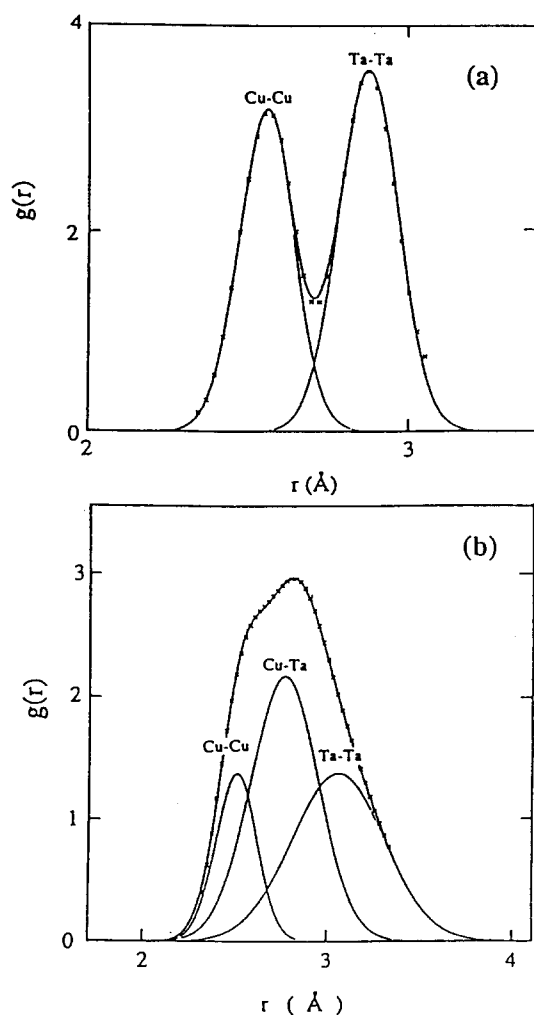
Table 1. Local atomic structure in amorphous Cu-Ta and Ni-Ta alloys.

Atom pair	Coordination number	Interatomic spacing (Å)	FWHM (Å)
$Cu_{30}Ta_{70}$ (MA 0 h)			
Cu-Cu	11.7	2.56	0.200
Ta-Ta	7.6	2.88	0.214
(Cu-Ta)		(2.72)*	
$Cu_{30}Ta_{70}$ (MA 120 h)			
Cu-Cu	4.6	2.51	0.259
Cu-Ta	8.3	2.77	0.429
Ta-Cu	3.5	2.77	0.429
Ta-Ta	8.3	3.06	0.577
$Ni_{30}Ta_{70}$ (MA 0h)			
Ni-Ni	11.4	2.50	0.191
Ta-Ta	7.3	2.87	0.198
(Ni-Ta)		(2.69)*	
$Ni_{30}Ta_{70}$ (MA 120h)			
Ni-Ni	5.0	2.53	0.235
Ni-Ta	6.6	2.76	0.419
Ta-Ni	2.7	2.76	0.419
Ta-Ta	9.3	3.04	0.622

* The value in the parenthesis is an average spacing of like atom pairs A-A and B-B and can be compared with the observed spacing of the A-B pair (underlined) in the amorphous state.
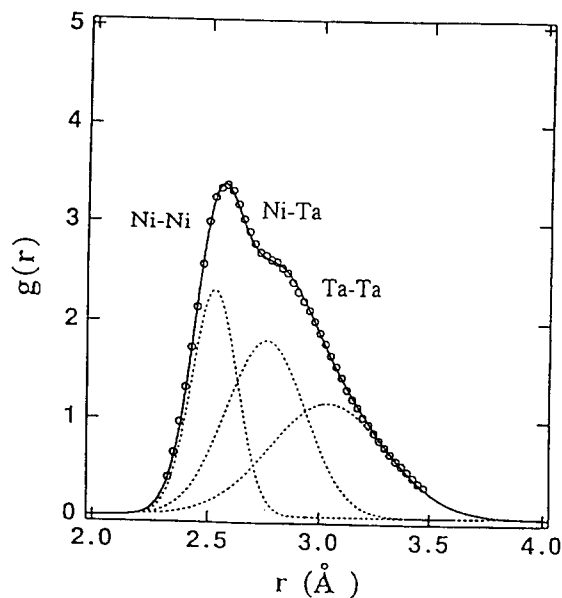
Fig.3. First peak of the total pair distribution function g(r) for the Cu:Ta=3:7 powders ((a): before milling, (b): after milling of 120 hour).

gaussian fitting are summarized in Table 1. The coordination number around Cu and Ta atoms becomes 12.9 and 11.8, respectively, in the amorphous phase. It is clear from Table 1 that the Ta-Ta distance substantially expands as a result of amorphization while the Cu-Cu distance remains essentially unchanged. We conclude from this analysis that the amorphization takes place by the penetration of smaller Cu atoms into the bcc Ta lattice.

The first peak in the pair distribution function

Fig.4. First peak of the total pair distribution function g(r) for the Ni:Ta=3:7 powders after milling of 80 hour.

g(r) for the $Ni_{30}Ta_{70}$ samples after the completion of amorphization is shown in Fig.4. The g(r) can be decomposed into the Ni-Ni, Ta-Ta and Ni-Ta correlations. Numerical data are also summarized in Table 1. A substantial expansion in the Ta-Ta distance is again

observed, while the Ni-Ni distance remains almost unchanged. In addition, we find that the half-width of the Ta-Ta distribution is much wider than that of the Ni Ni distribution. Surprisingly, all these features coincide well with those observed in the Cu-Ta. Thus, we believe that the local atomic structure in the amorphous Ni-Ta is essentially the same as that in the amorphous Cu-Ta, regardless of the difference in the sign of heat of mixing and that the elementary process involved in amorphization should be common to both systems; the penetration of smaller atoms Ni and Cu into the bcc Ta crystal.

4. Conclusion

The mechanical alloying has been carried out on the two Ta-based alloy systems. The combination of Ni Ta is characterized by a negative heat of mixing, whereas that of Cu-Ta a positive heat of mixing. The neutron diffraction measurement have been employed to analyze the structural changes taking place during milling. An amorphous phase was formed in all two cases. The local atomic structure in the amorphous Cu-Ta is compared with that in the amorphous Ni-Ta with a large negative heat of mixing. We conclude that, in spite of the difference in the sign of heat of mixing, the local atomic structure in the amorphous Ni Ta is essentially the same as that in the amorphous Cu-Ta. The elementary process toward the amorphization is found to be common in both systems and to be described as the preferential penetration of smaller atoms Cu or Ni into the crystallites of bcc Ta.

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