Mechanical Alloying Effect in Immiscible Cu-Based Alloy Systems.

Chung-Hyo Lee, Seong-Hee Lee, Ji-Soon Kim* and Young-Soon Kwon*

Dept. of Advanced Materials Science & Engineering, Mokpo National University, Muan 534-729, Korea
*Research Center for Machine Parts and Materials Processing, University of Ulsan, Ulsan 680-749, Korea

Abstract The mechanical alloying effect has been studied on the three Cu-based alloy systems with a positive heat of mixing. The extended bcc solid solution has been formed in the Cu-V system and an amorphous phase in the Cu-Ta system. However, it is found that a mixture of nanocrystalline Cu and Mo is formed in the Cu-Mo system. The neutron diffraction has been employed as a main tool to characterize the detailed amorphization process. The formation of an amorphous phase in Cu-Ta system can be understood by assuming that the smaller Cu atoms preferentially enter into the bcc Ta lattice during ball milling.

Keywords : Mechanical alloying, Immiscible alloy system, Positive heat of mixing, Copper-tantalum, Copper-vanadium, Amorphization, Extended solid solution, Neutron diffraction, Structure factor

1. Introduction

The solid-state amorphization by mechanical alloying has been considered to be driven by two possible mechanism: one is an energetically down-hill process driven by chemical reaction at the interface between the two adjacent layers and the other an energetically up-hill process driven by accumulating defects and grain refinement[1-4]. Only the latter process is believed to be responsible for the amorphization of a stable intermetallic compound subjected to mechanical alloying[2]. 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 apparently exist in this case.

Many binary alloy systems consisting of Cu and transition metal elements like Ta, V and Mo are characterized by a positive heat of mixing, ΔH_{mix}[5]. For example, the ΔH_{mix} of Cu-Ta, Cu-V and Cu-Mo systems are theoretically predicted to be +2 kJ/mole, +5 kJ/mole and +19 kJ/mole, respectively. A equilibrium phase diagram shows that the Cu-V system forms only a very limited solid solution and dissociates into two immiscible liquids at elevated temperatures, while the Cu-Ta system forms essentially no solid solution over a whole concentration range. In case of Cu-Mo system, neither solid solution nor compound exists and even liquid partitions into two phases at elevated temperature[6]. This is the reflection of a large positive heat of mixing. It is therefore of interest to study to what extent the mechanical alloying is capable of producing a metastable phase with increasing the heat of mixing. We report on the mechanical alloying effect in the Cu-Ta, Cu-V and Cu-Mo as representatives of systems with a positive heat of mixing. Evidences for the formation of an amorphous phase in the Cu-Ta and an extended solid solution in the Cu-V after mechanical alloying are presented.

2. Experimental Procedure

The mechanical alloying was carried out at room temperature in an argon gas atmosphere, using a mixture of pure Cu (99.9%, <150 μm in size), Ta (99.9%, <50 μm in size), V (99.5%, <50 μm in size) and Mo (99.9%, <3 μm in size) powders. Pure metal powders were mixed so as to have following average atomic compositions: $Cu_{30}Ta_{70}$, $Cu_{30}V_{70}$ and $Cu_{30}Mo_{70}$. A planetary-type ball mill (Fritsch Pulverisette 5) was used with its intensity of 5. The vial and balls made of Cu-Be (1.8−2.0 at.% Be) alloy were used to avoid iron contamination. The total mass of powders was about 20 g and the ratio of balls to powders was 7:1.

The thermal properties for samples after various

milling times have been studied by differential scanning calorimetry (DSC) in combination with ordinary X-ray diffraction with Cu-Kα radiation. A detailed structural change at various stages of mechanical alloying was studied by neutron diffraction. The neutron diffraction spectra were measured, using High Intensity Total (HIT) scattering spectrometer at High Energy Physics Laboratory, Tsukuba, Japan. The method and data analysis for the neutron diffraction used in this study have been reported elsewhere[7].

3. Results and Discussion

The X-ray diffraction spectra are shown in Fig. 1 as a function of milling time for $Cu_{30}Ta_{70}$ and $Cu_{30}V_{70}$
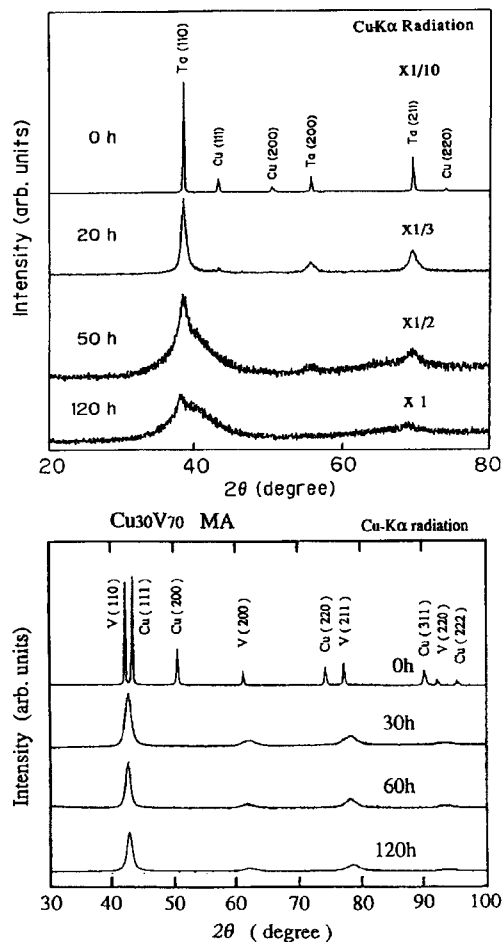

Fig. 1. X-ray diffraction spectra for the $Cu_{30}Ta_{70}$ and $Cu_{30}V_{70}$ powders subjected to mechanical alloying for various time intervals.

powders. It can be seen that the diffraction lines of Cu in both Cu-Ta and Cu-V system disappear first while those of Ta or V remain essentially unchanged within 30 h of milling. When milling is further continued, however, a noticeable difference is seen in the diffraction lines of the early transition metal elements. The vanadium apparently maintains its bcc structure even after 120 h of milling, though the position of each peak is slightly shifted to higher angles. In contrast, the Ta lines in the Cu-Ta system substantially broaden and approach a halo-like pattern when milling time reaches 50–120 h, suggesting that an amorphous phase is slowly formed[8]. Also, it is found that the milling of a mixture of $Cu_{30}Mo_{70}$ up to 200 h could reduce an average grain size of both pure Cu and Mo particles to less than 10 nm without any evidence for the formation of solid solution. The electron diffraction and TEM observation have shown no change in the lattice constant of pure Cu and Mo.

The corresponding DSC spectra for Cu-Ta and Cu-V were measured. Only a broad heat evolution is observed in the $Cu_{30}V_{70}$ powders. As is clear from Fig. 2, however, the DSC spectra for the $Cu_{30}Ta_{70}$ powders exhibit a sharp exothermic peak at about 550°C after 120 h of milling. The X-ray diffraction analysis after
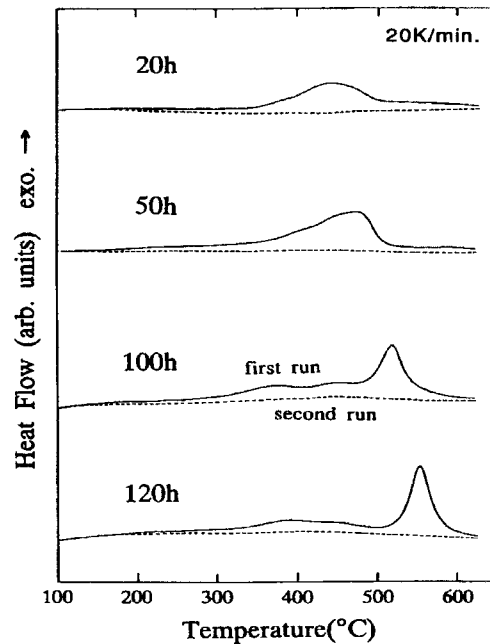

Fig. 2. The DSC spectra for the $Cu_{30}Ta_{70}$ powders subjected to mechanical alloying for various time intervals.

the first DSC run revealed a complete decomposition into pure elements Cu and Ta without formation of any other compounds. 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 ΔH_t accumulated during milling. It is seen that the value of ΔH_t tends to saturate at the value of 12 kJ/mol in $Cu_{30}Ta_{70}$ powders. It happens that the value is close to the calculated free energy of 11 kJ/mol necessary to transform a mixture of $Cu_{30}Ta_{70}$ powders into an amorphous phase[9]. Hence, it is thermodynamically possible to assume the formation of an amorphous phase in this system.

A neutron diffraction experiment was carried out to get detailed information about the structural change and local atomic structure. The total structure factor $S(Q)$ for the $Cu_{30}V_{70}$ powders after various milling times was measured. The $S(Q)$ for the Cu-V system represents essentially the Cu-Cu correlation because the coherent scattering length of the V atom in the neutron diffraction is negligibly small. The fcc-Cu peaks in the spectrum change with milling time and those after 120 h of milling can be indexed in terms of the bcc-Cu with the lattice constant of 2.97A. Fig. 3 shows the structure factors, $S(Q)$, of a series of the $Cu_{30}Ta_{70}$ powders after various milling times[8]. Bragg peaks associated with fcc-Cu and bcc-Ta are resolved in $S(Q)$ before milling. However, the Cu lines disappear first with increasing milling time and the profile approaches that typical of an amorphous phase after 120 h of milling, being consistent with the X-ray dif-
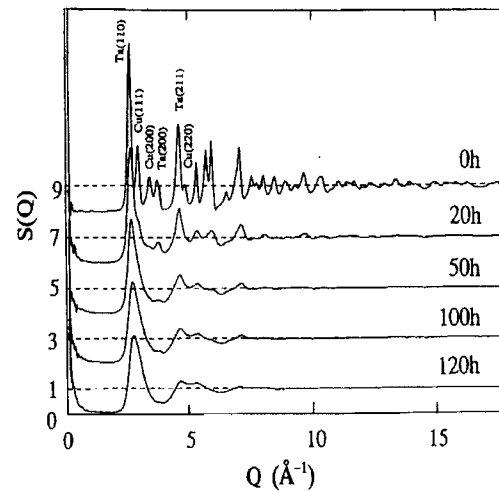

Fig. 3. Total structure factor for the $Cu_{30}Ta_{70}$ powders to mechanical alloying for various time intervals.

fraction data. The (200) diffraction peaks correspond to the second nearest neighbor atoms in both fcc Cu and bcc Ta. Fig. 3 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[10].

It is of great interest, at this stage, to evaluate a change in the local atomic environments around Cu and Ta atoms due to ball milling by analyzing the first
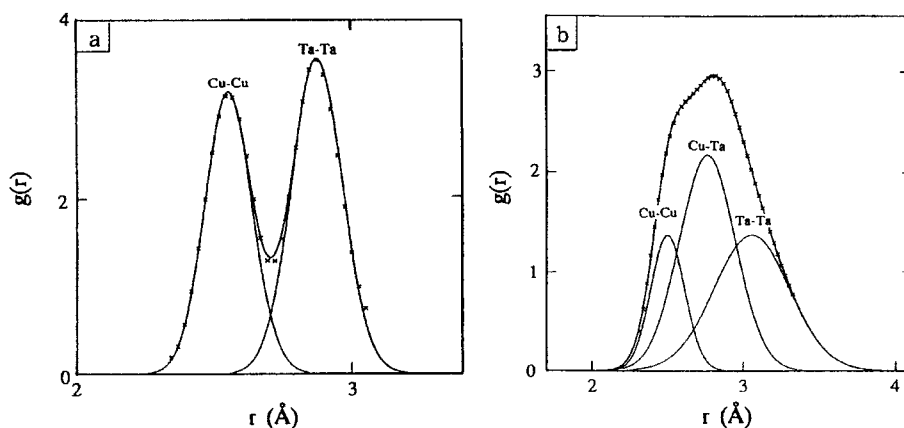

Fig. 4. First peak of the total pair distribution function, g(r) for the $Cu_{30}Ta_{70}$ powders (a) before milling and (b) after milling of 120 h.

Table 1. Local atomic structure in amorphous Cu-Ta alloy

Atomic pairs	Coordination number	Interatomic spacing (Å)	FWHM (Å)
MA 0 h			
Cu-Cu	11.7	2.56	0.200
Ta-Ta	7.6	2.88	0.214
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

nearest neighbor peak of the total pair distribution function g(r) for the sample before ball milling and that after 120 h-milling[8]. The results for the Cu-Ta system are shown in Fig. 4. 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. 4(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 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. 4(b). The numerical results obtained by 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.

4. Conclusions

The present work clearly shows that an amorphous phase is formed by mechanical alloying in the Cu-Ta

system and a supersaturated solid solution in the Cu-V system. Also, a mixture of nanocrystalline Cu and Mo with nano-sized grains is obtained in the Cu-Mo system. Admittedly, it is concluded that all these findings are the reflection of the different value of ΔH_{mix} in immiscible Cu based systems.

Acknowledgments

References

1. R. B. Schwarz and W. L. Johnson: Phys. Rev. Lett., **51** (1983) 415.
2. R. B. Schwarz and C. C. Koch: Appl. Phys. Letters, **49** (1986) 146.
3. R. B. Schwarz, R. R. Petich and C. K. Saw: J. Less-Common Met., **76** (1985) 171.
4. C. H. Lee, M. Mori and U. Mizutani: J. Non-Cryst. Solids, **117-118** (1990) 733.
5. F. R. Boer, R. Boom, W. C. Matten, A. R. Miedema and A. K. Niessen: Cohesion in Metals, North-Holland, Amsterdam (1988) 143.
6. T. B. Massalski: Binary Alloy Phase Diagrams, 3rd ed., American Society for Metals, Seto (1990) 1485.
7. T. Fukunaga: Bul. Jpn. Inst. Met., **26** (1987) 481.
8. C. H. Lee, M. Mori, T. Fukunaga and U. Mizutani: Mater. Sci. Forum, **88-90** (1992) 399.
9. A. R. Miedema and A. K. Niessen: Suppl. to Trans. JIM, **29** (1988) 209.
10. T. Fukunaga, Y. Homma, M. Misawa and Y. Suzuki: J. Non-Cryst. Solids, **117-118** (1990) 721.