

기계적 합금화에 의한 비정질 Cu-Ta 분말의 제조 및 전자물성

이충효 · 朝比奈正 · 水谷宇一郎*

通産省 工業技術院
*名古屋大學 工學部

Formation and Electronic Properties of the Amorphous Cu-Ta Alloy Powders Subjected to Mechanical Alloying

Chung-Hyo Lee, Tadashi Asahina and Uichiro Mizutani*

Materials Processing Department, National Industrial Research Institute of Nagoya,
Hirate-cho, Kita-ku, Nagoya, Japan

*Department of Crystalline Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

초 록 저자들은 최근 비고용 Cu-Ta계의 기계적 합금화(Mechanical Alloying)방법을 이용하여 이계에 있어서 비정질상의 형성에 대한 구조적 확인을 중성자 회절과 EXAFS(Extended X-ray Absorption Fine Structure)의 실험결과로부터 얻었다. Cu-Ta계와 같이 혼합 엔탈피(Heat of Mixing : ΔH_{mix})가 정인계에 있어서 비정질상 형성에 대한 연구는 구조적인 측면 뿐만 아니라, 시료의 전자물성에 대해서도 많은 연구가 되어야만 할 것으로 사료된다.

따라서 본 논문에서는 120시간 MA방법으로 제작한 시료에 대하여 초전도 천이온도 및 X선 광전자분광 실험에서 얻은 가전자대 구조의 전자물성을 측정하고, 그 결과로부터 이종원자 Cu와 Ta간의 결합은 화학결합에 의한 생성임을 확인하였는데, 이들 결과로부터 120시간 MA를 행하여 얻어진 시료는 확실하게 비정질 합금임을 알 수 있었다.

Abstract We recently showed from the neutron diffraction and extended X-ray absorption fine structure studies the structural evidence for the formation of an amorphous phase in immiscible Cu-Ta system subjected to mechanical alloying. In a system with a positive heat of mixing like Cu-Ta, we consider it necessary to confirm the formation of an amorphous phase not only from the structural studies but also from a change in the electronic properties. We show the electronic evidence for the formation of the chemical bonding between the unlike atoms Cu and Ta for the 120 h-milling sample through changes in superconducting transition temperature and X-ray photoemission spectroscopy valence band structure.

I. Introduction

Recently a considerable amount of work has been performed on the solid-state amorphization process due to mechanical alloying (MA)¹⁻³. In addition, the MA under a reactive gas atmosphere has also been reported to produce an amorphous phase through the solid-gas reaction^{4,5}. The amorphization in the solid state reaction has been considered to be driven by two possible processes⁶: 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 the grain refinement. Only the latter process is believed to be responsible for the amorphization of an intermetallic compound and a mixture of two different pure metals with a positive heat of mixing ΔH_{mix} ⁷⁻¹¹, since no chemical driving force is expected in both cases. Therefore, it is of great interest to

study if the solid state amorphization proceeds through the latter process in a system with a positive heat of mixing like Cu-Ta system. Indeed, we found the formation of an amorphous phase in the Cu-Ta powders subjected to ball milling at 300K, which has been evidenced from the structural analyses based on the neutron diffraction and extended X-ray absorption fine structure(EXAFS) measurements^{12,13}. The formation of an amorphous phase from the point of view of thermodynamics has been also discussed^{8,14}. The conclusion for the amorphization should be cautiously drawn in a system with a positive heat of mixing ΔH_{mix} , since no chemical driving force is apparently expected to be available. In the present paper, we discuss the amorphization process from the viewpoint of the electronic states by comparing the low-temperature specific heats and X-ray photoemission spectroscopy(XPS) valence band profiles for a 3 : 7 mixture of pure Cu and Ta powders before and after mechanical alloying.

II. Experimental Procedure

The ball milling was carried out at room temperature for a mixture of pure Cu(99.9%, 150 μm in size) and Ta(99.9%, 50 μm in size) powders with an atomic ratio 3 : 7. A planetary ball mill(Fritsch Pulverisette 5) was used with its intensity 5. The vial and balls are made of the Cu-Be(1.8-2.0 at.% Be) alloy. The total mass of powders was about 20g and the ratio of balls to powders was 7 : 1. The structure of ball-milled powders was studied by X-ray diffraction with Cu-K α radiation (RIGAKU, RAD-II C). The thermal analysis was made using a differential scanning calorimetry(DSC, RIGAKU-8131BH) apparatus with a heating speed of 20 $^{\circ}\text{C}/\text{min}$.

The low-temperature specific heat was measured in the temperature range 1.5-6.0K, using an ordinary adiabatic method. The powder sample was compacted in a gold-plated Cu container, the heat capacity of which has been

subtracted from the total. A total weight of each sample was about 2.5g. Small amount of Cu powders, the contribution being subtracted likewise, had to be added for the ball milled sample to ensure a good thermal contact and to attain an immediate thermal equilibrium after each heating in the specific heat run.

The Cu-Ta powders before and after milling were embedded into a pure indium disc for the X-ray photoemission(XPS) measurement. The core levels and the valence band profiles were measured, using a monochromatic Al-K α radiation(Surface Science Instruments, SSX-100). The surface of the sample was sputtered by the Ar ions for about 5 hours to remove the oxide layer prior to XPS measurements. Signals for obtaining the valence band profile were accumulated for about 12 hours.

III. Results and Discussion

The X-ray diffraction spectra are shown in Figure 1 as a function of milling time for the Cu-Ta powders. It can be seen that the dif-

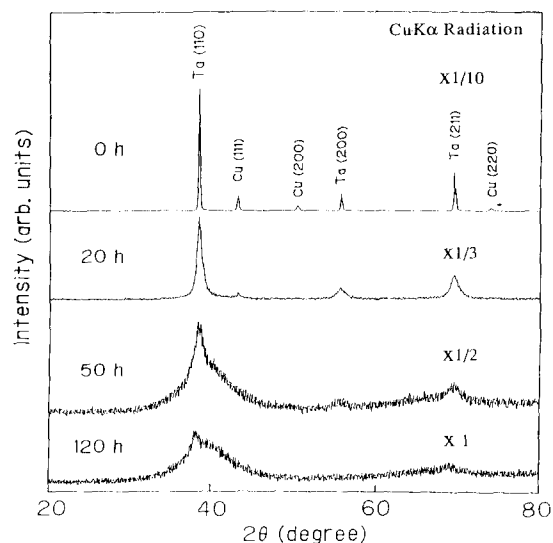


Fig. 1. X-ray diffraction spectra for a 3 : 7 mixture of Cu-Ta powders ball-milled for different time intervals. A scale for the intensity for the powders before ball milling (0 h) is reduced to 1/10 times as large as that for other data.

fraction lines associated with Cu disappear first and the remaining Ta lines gradually approach a halo-like pattern with increasing milling time. The corresponding DSC spectra are shown in Figure 2. The DSC run was taken up to 630°C with subsequent cooling to room temperature. The X-ray diffraction analysis revealed a complete decomposition into pure Cu and Ta after the DSC run. The second run was made for each sample to determine the base line, as shown in Figure 2. The DSC spectra for the sample ball-milled for less than 50h exhibit a broad exothermic heat evolution. In contrast, the sample ball-milled for 120h is characterized by a sharp peak at about 560°C, which can be identified as arising from the crystallization of the amorphous phase.

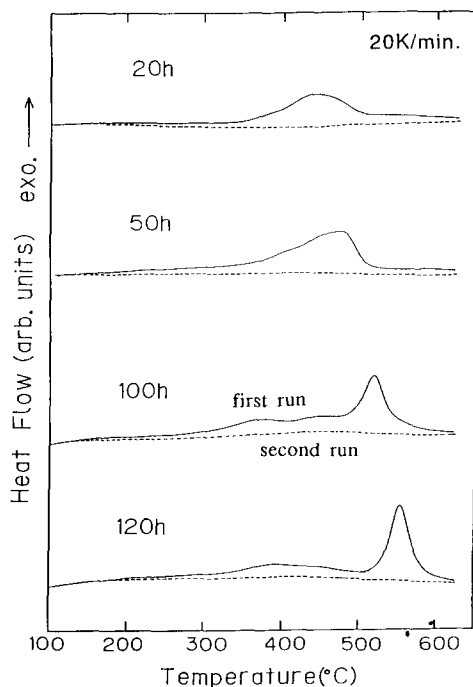


Fig. 2. The DSC spectra for a 3 : 7 mixture of Cu-Ta powders ball-milled for different time intervals. Solid and dotted curves represent the first and second runs, respectively.

Now we discuss the effect of milling on the low-temperature specific heat of the Cu-Ta powders. Figure 3 shows the C/T versus T^2

data for a 3 : 7 mixture of elemental powders Cu and Ta. Included are the data for the powders after 120h-milling and those with a subsequent heat treatment at 800°C for 10h in vacuum. It is clear that the superconducting transition has been completely suppressed after 120h-milling but is recovered after the heat treatment. The corresponding X-ray diffraction spectra are shown in Figure 4. The formation of an amorphous phase can be seen for the powders after 120h-milling. It is also seen that the amorphous phase decomposes into pure Ta and Cu after the heat treatment at 800°C. We believe that the complete suppression of the superconducting transition after milling is due to the alloying effect.

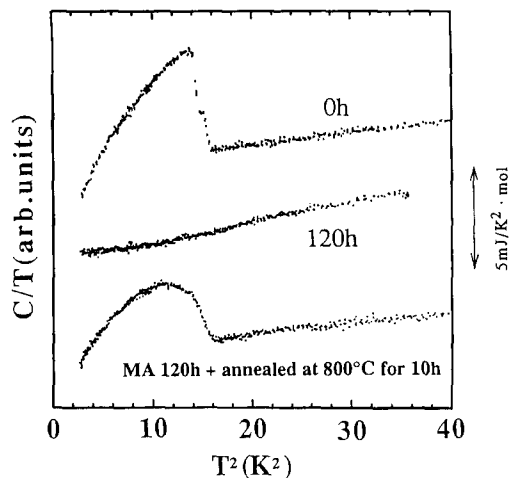


Fig. 3. Low-temperature specific heats in the form of C/T versus T^2 for a 3 : 7 mixture of Cu and Ta powders prior to milling (0h), after 120h-milling (120h) and that with a subsequent heat treatment at 800°C for 10h. A specific heat jump for the sample before milling reflects the superconductivity of pure Ta. It is suppressed when an amorphous phase is formed, but recovers after the heat treatment.

To strengthen our argument, we present one additional specific heat data for the Cu-Zr system, where the heat of mixing is known to be negative and the formation of an amorphous phase has been confirmed by various

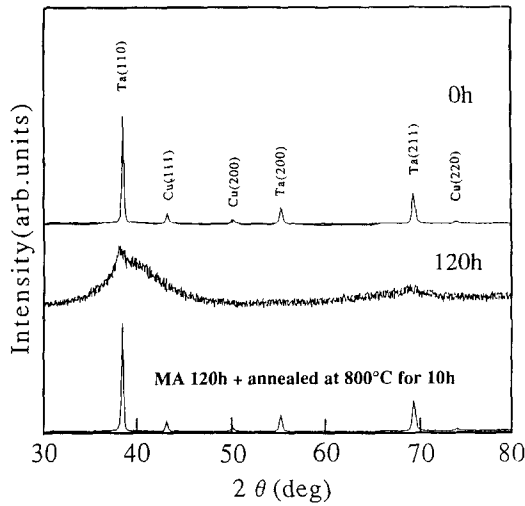


Fig. 4. X-ray diffraction spectra with Cu-K α radiation for a 3 : 7 mixture of Cu and Ta powders subjected to ball milling. Samples are the same as those employed for the specific heat measurements.

methods including mechanical alloying¹⁵⁾ Figure 5 shows the X-ray diffraction patterns

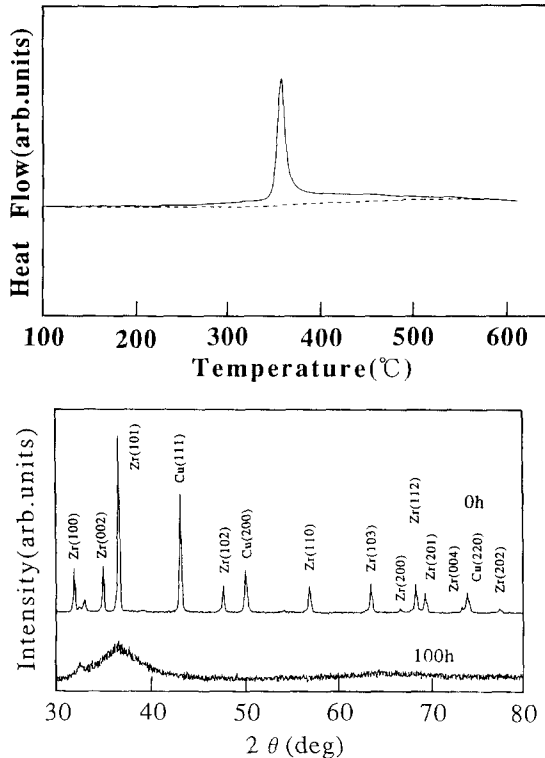


Fig. 5. (a) X-ray diffraction patterns and (b) DSC spectra for a 2 : 8 mixture of Cu and Zr powders mechanically alloyed for 0h and 100h.

coupled with the DSC data for a 2 : 8 mixture of Cu and Zr prior to milling and after 100h-milling. A combination of the X-ray diffraction pattern and the corresponding DSC data for the sample after 100h-milling leads us to conclude that an amorphous phase has been formed and an exothermic peak at about 360 °C corresponds its crystallization. The Zr-oxide, being unavoidably present in the starting Zr metal powders, yields the diffraction peak at $2\theta = 32.5^\circ$ and remains finite for the 100h-milling sample. We believe that the Zr-oxide is apparently intact in the MA process. The corresponding C/T versus T^2 data are shown in Figure 6. The superconducting transition temperature(T_c) of pure Zr is only 0.5K and, hence, cannot be observed in the present experimental setup. As shown in Figure 6, however, the superconducting transition appears for the 100h-milling sample, the structure of which is identified as an amorphous phase by X-ray diffraction and DSC. The value of T_c is known to be distributed over 0.3 -3.2K in the amorphous Cu-Zr alloys¹⁶⁾. Hence, Figure 6 lends a support to our approach that

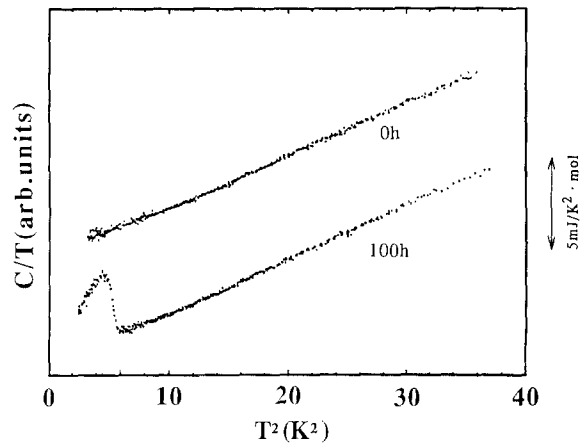


Fig. 6. Low-temperature specific heats in the form of C/T versus T^2 for a 2 : 8 mixture of Cu-Zr powders prior to milling (0h) and after 100h-milling(100h). No superconductivity is observed for the former, since its transition temperature of pure Zr is only 0.5K. A specific heat jump for the latter is due to superconducting transition of the amorphous phase.

the formation of the chemical bonding can be monitored by a change in the superconducting transition temperature observed in the low temperature specific heat.

The effect of milling on the Cu-Ta powders was also studied by the photoemission spectroscopy measurements. The Ta-4d core level after milling has been shifted by 0.3eV to a higher binding energy. More dramatic change has been observed in the valence band structure. The valence band spectra for the samples before milling and after 120h-milling, both being identical to those employed for the specific heat measurements, are shown in Figure 7. The spectrum before milling can be ex-

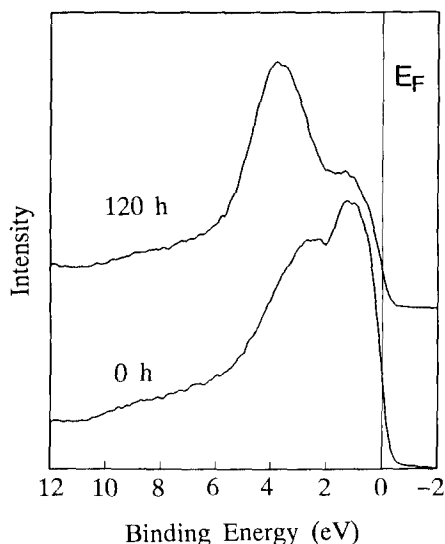


Fig. 7. XPS valence band profiles for a 3 : 7 mixture of Cu-Ta powders prior to milling (0h) and after 120h-milling. The former corresponds to the superposition of the d-bands of pure Cu and pure Ta, whereas the latter to the amorphous phase.

plained as a superposition of the 3d-band of pure Cu and the 5d-band of pure Ta. The valence band is found to change drastically after 120h-milling. The valence band structure of an amorphous binary alloy composed of the early transition(TE) metal and the late transition(TL) metal is known to consist of a two-peaked split band, the d-band of the TE metal

appearing near the Fermi level and that of the TL metal at higher binding energy¹⁷⁾. The spectrum after milling is characteristic of such amorphous TE-TL alloys : the peak near E_F can be assigned to the Ta 5d-band and that at a higher binding energy to the Cu 3d-band. It is seen that the center of the Cu-3d band after milling is shifted by about 1eV towards a higher binding energy relative to that of pure Cu. This agrees well with the corresponding shift reported for the amorphous Cu-Zr alloys¹⁷⁾. We conclude, therefore, that the substantial change in the valence band structure reflects the formation of the chemical bonding between unlike elements Cu and Ta in spite of the possession of a positive heat of mixing.

IV. Conclusion

We have revealed that the $\text{Cu}_{30}\text{Ta}_{70}$ amorphous powders can be produced by mechanical alloying process, as demonstrated by X-ray diffraction, DSC analysis and by the electronic studies through a change in the superconducting transition in the low-temperature specific heat and the XPS valence band structure. By combining with the neutron diffraction and EXAFS studies, we reach our conclusion that the Cu-Ta system can be apparently amorphized by mechanical alloying, despite the fact that the atomic pair of which is immiscible.

References

1. L. Schultz, *J. Less-Common Met.*, **145**, 233 (1988).
2. R. B. Schwarz, R. R. Petrich and C. K. Saw, *J. Non-Cryst. Solid* **76**, 281(1985).
3. U. Mizutani and C. H. Lee, *J. Mat. Sci.* **25**, 399(1990).
4. A. Calka and J. S. Williams, *Mat. Sci. Forum* **88-90**, 787(1992).
5. K. Sakurai, C. H. Lee, N. Kuroda, T. Fukunaga and U. Mizutani, *J. Appl. Phys.* **75**, 7752(1994).
6. W. L. Johnson, *Prog. Mat. Sci* **30**, 81

- (1986).
7. R. B. Schwarz and C. C. Koch, *Appl. Phys. Lett.*, **49(3)**, 146(1986).
 8. C. H. Lee, T. Fukunaga and U. Mizutani, *Mat. Sci. Eng.* **A134**, 1334(1991).
 9. C. H. Lee, M. Mori and U. Mizutani, *J. Non-Cryst. Solids*, **117/118**, 733(1990).
 10. T. Koyano, C. H. Lee, T. Fukunaga, U. Mizutani, S. Ikeda, E. Kita and A. Tasaki, *J. Magn. Magn Mater* **126**, 161(1993).
 11. C. H. Lee, T. Fukunaga and U. Mizutani, *J. Korean Inst. of Met. & Mater.* **31**, 193 (1993).
 12. T. Fukunaga, K. Nakamura, K. Suzuki and U. Mizutani, *J. Non-Cryst. Solids* **117/118**, 700(1990)
 13. K. Sakurai, Y. Yamada, M. Ito, C. H. Lee, T. Fukunaga and U. Mizutani, *Appl. Phys. Lett.* **57**, 2660(1990).
 14. C. H. Lee, M. Mori, T. Fukunaga and U. Mizutani, *Jpn. J. Appl. Phys.* **29**, 540 (1990).
 15. C. C Koch, *J. Non-Cryst. Solids* **117/118**, 670(1990).
 16. Z. Altounian and J. O. Strom-Olsen, *Phys. Rev.* **B27**, 4149(1983).
 17. P. Oelhafen, E. Hauser and H. J. Güntherodt, *Solid State Commun.* **35**, 1017 (1980).