ESOMAT 2009, 02011 (2009)
DOI:10.1051/esomat/200902011

Aging effect on martensitic transformation at cryogenic temperatures in Cu-Al-Mn alloy

S. Ii[a], K. Tsuchiya, T. Koyano[1]

National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
[1] Cryogenic division, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan

Abstract. Aging effect on martensitic transformation in $Cu_{83-X}Al_{17}Mn_X$ shape memory alloys (X = 10,12,14,16 and 18) have been investigated by electrical resistivity (ER) and differential scanning calorimeter (DSC) measurements. In $Cu_{71}Al_{17}Mn_{12}$ aged at 373 K for 0.6 ks, we found that martensitic transformation occurred at around 100K in ER measurement. It was also confirmed that the transformation temperatures increased with aging temperature and time. In addition, an enthalpy of reverse transformation increased with aging temperature, but it exhibited no systematic dependence on the aging time. The enthalpy of reverse transformation in $Cu_{71}Al_{17}Mn_{12}$ alloy aged at 473K for 0.6ks (As = 200 K), was estimated to be about 150 J/mol by DSC measurements, which is nearly equal to that in Cu-Al-Mn alloy transformed at around room temperature.

1. INTRODUCTION

Many Cu-based β-phase alloys exhibit thermoelastic martensitic transformation and have been one of promising materials as shape memory alloys because of low cost compared to Ti-Ni shape memory alloy [1]. But, since the Cu-based shape memory alloys have huge elastic anisotropy and are very brittle [2], it was difficult to apply the polycrystalline Cu-based shape memory alloys to an engineering field. Recently, Kainuma *et al*. have been developed ductile β-phase Cu-Al-Mn alloys exhibiting the superelastic properties at around room temperature based on the controlling of their degree of order and texture [3-6] and applied to the medical field [6]. Another important character of the Cu-Al-Mn alloys is that the thermoelastic martensitic transformation below liquid nitrogen temperature (77K) was reported by Prado [7], although Ti-Ni alloys with near equi-atomic composition known as typical shape memory and superelastic alloys does not exhibit martensitic transformation below 100K [8]. Therefore, this suggests that the Cu-Al-Mn alloys are one of promising cryogenic shape memory alloys. On the other hand, martensitic transformation of Cu-based shape memory alloys is strongly affected by aging because of the migration and annihilation of quenched-in vacancies causing a change in long and/or short range ordered structures [9, 10]. So far, the aging effect of Cu-based shape memory alloys is widely investigated by many researchers. However, there is no systematic examination of the Cu-Al-Mn alloy. In this study, we have investigated aging effect on the martensitic transformation around cryogenic temperature in Cu-Al-Mn alloys

2. EXPERIMENTAL PROCEDURE

In this study, we have prepared the $Cu_{83-X}Al_{17}Mn_X$ alloys by induction melting in an argon atmosphere. The chemical compositions of alloys used in this study are summarised in Table 1. Hereafter, we designated the alloy by the composition of Mn (e.g., 10Mn). Obtained five alloy ingots were hot-rolled at 1173 K to sheets of 1 mm thick and cold-rolled to the thickness of 0.5mm. The obtained sheets were spark cut into the strips of 2 x 10 x 0.5 mm for electrical resistivity (ER) measurement and the 2 x 2 x 0.5 mm for differential scanning calorimeter (DSC) measurement. The specimens for ER and DSC measurements were solution treated at 1173 K for 0.6 ks in air and water quenched and aged at 373 K, 423 K, 448 K and 573 K for 0.06 to 7.2 ks, respectively. The ER and DSC measurements were conducted to measure the transformation temperatures and heat flow. ER was measured from room temperature to 5 K with the heating and cooling rate of 1.67×10^{-2} K/sec. DSC measurements were carried out on Perkin Elmer Diamond DSC to 80K with heating and cooling rate of 0.167 K/sec. Some of the specimens were aged at various temperatures for 0.06ks to 7.2ks in DSC and measured

[a] e-mail: II.Seiichiro@nims.go.jp

Article available at http://www.esomat.org or http://dx.doi.org/10.1051/esomat/200902011

Table 1 Chemical composition of Cu-Al-Mn alloys (at%).

	Cu	Al	Mn
10Mn	73	17	10
12Mn	71	17	12
14Mn	69	17	14
16Mn	67	17	16
18Mn	65	17	18

transformation temperature without removing outside after aging for a certain period in DSC.

3. RESULTS AND DISCUSSION

Fig. 1 shows normalized ER curves of five kinds of Cu-Al-Mn alloys aged at 373K for 0.6ks after solid solution treatment. In the curve obtained from 10Mn, no clear change in electrical resistivity with martensitic transformation. This is due to that the martensitic temperature is around room temperature, and it is inferred that martensitic transformation occurred during the quench into water. In fact, the exo- and endothermic peaks with martensitic transformation are detected around 323K by DSC measurement and it is consistent with the result reported by Kainuma *et al*. [3]. The drastic change in ER due to forward and reverse martensitic transformation during cooling and heating cycles were clearly observed in the curve for 12Mn. The transformation temperatures are determined to be M_s: 117 K, M_f: 97 K, A_s: 114 K and A_f: 121K. It is suggested that the 12Mn can be a candidate for shape memory alloys working at around 100K. On the other hand, there is no change in ER in the other alloys containing Mn composition of above 14at%. Those alloys aged in above condition do not transform to 5K. In order to measure the transformation behaviour and enthalpy with aging by DSC, we investigated the aging effect on martensitic and reverse transformations and transformation enthalpy for 12Mn.

Fig.2 shows DSC curves of 12Mn aged at 473K for various time from 0.06 ks to 7.2 ks, respectively. The curves exhibited an upward peaks corresponds to martensitic transformation on cooling and downward peaks to reverse transformation on heating process, respectively. The many exothermic peaks also can be clearly seen in every cooling curve except for as quenched specimen. These multiple peaks can be detected in acoustic emission (AE) and DSC measurements in other Cu-based shape memory alloys [11,12]. Probably, the multiple peaks with martensitic transformation are due to quenched–in vacancies related to pinning effect of interface movement. On the other hand, the endothermic peak for the reverse transformation on heating is a single and very smooth. The difference between exo- and endothermic peak is considered to be due to whether the strain is stored or relieved by each transformation. In this study, since the determination of martensitic transformation temperatures by the DSC is difficult, so that we focus on the reverse transformation temperatures, *i.e,* A_s and A_f. Fig.3 shows an aging time dependence of the reverse transformations with aging temperatures of 423 K, 448 K and 473 K. As clearly seen, reverse transformation temperatures are increased with aging time. A_s and A_f saturated at around 200K and 210K irrespective of different aging temperatures. In addition, the reverse transformation temperature of the specimen aged for short time strongly depends on the aging temperature. We have also measured the enthalpy of reverse transformation in 12 Mn alloys from the results of the DSC measurements as shown in Fig.2. Fig.4 shows an aging temperature and time dependence of enthalpy of

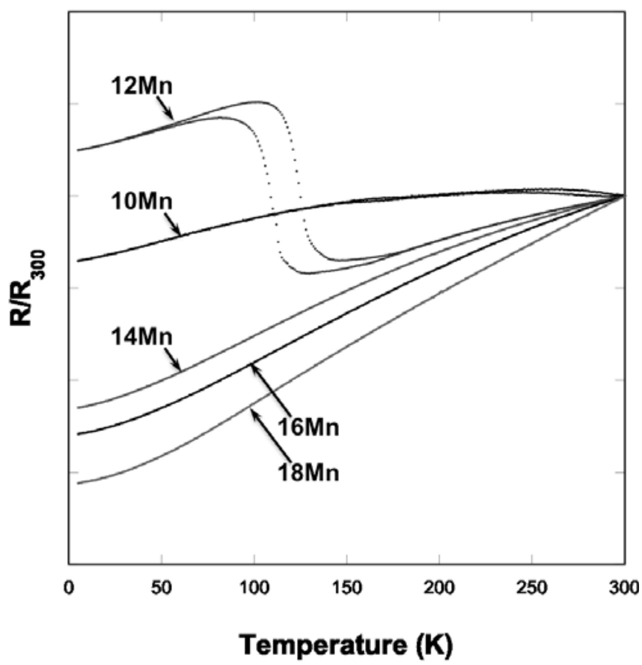

Fig.1. Normalized electriocal resistivity curves of Cu-Al-Mn alloys aged at 373K for 0.6ks after solution treatment.

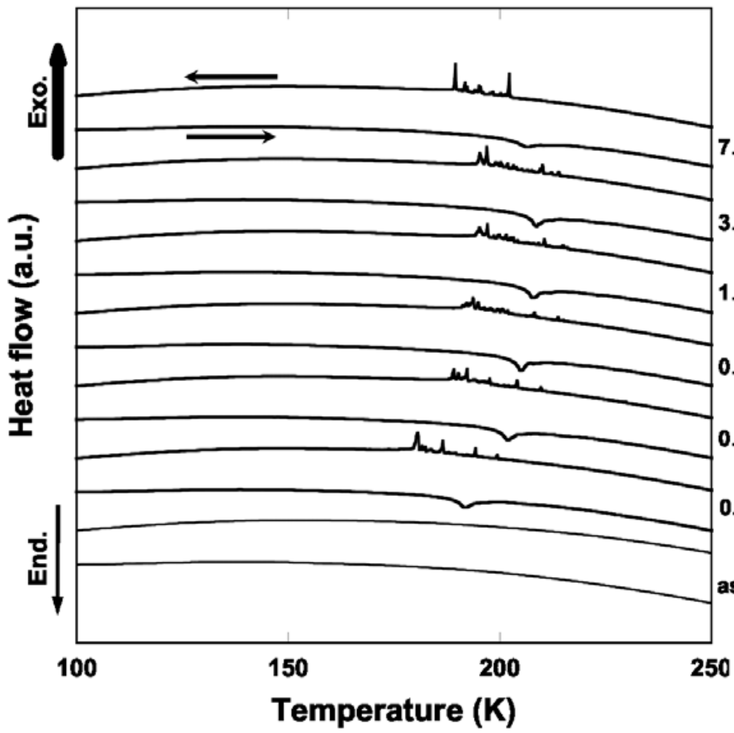

Fig.2. DSC curves of $Cu_{71}Al_{17}Mn_{12}$ alloy aged at 473K for verious time shown in right side of each curve.

reverse transformation in 12Mn alloys. In this figure, the enthalpies of the specimen, which are aged at 423K, 448K and 473K are 50, 120 and 150 J/mol, respectively. And it increases with aging temperature. The enthalpy in the specimens aged at 423K exhibits a constant value of approximately 50 J/mol and is independent of the aging time. On the other hand, that of the specimens aged at 448K and 473K slightly increased with the aging time. Comparing the results with Fig.3, although the reverse transformation temperature reaches to the almost same level in the specimen aged at 423K for 3.6ks and at 473K for 0.3ks, the enthalpy of the specimen aged at 473K is larger than that of the specimen aged at 423K. We have clarified that the enthalpy of the reverse

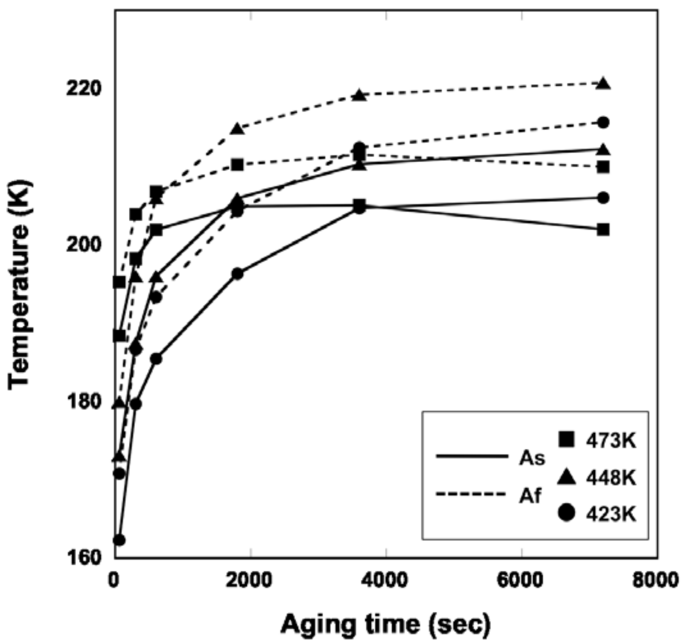

Fig.3. Aging time dependence of reverse transformation températures of $Cu_{71}Al_{17}Mn_{12}$ alloy aged at 423K(●), 448K(▲) and 473K(■), respectively.

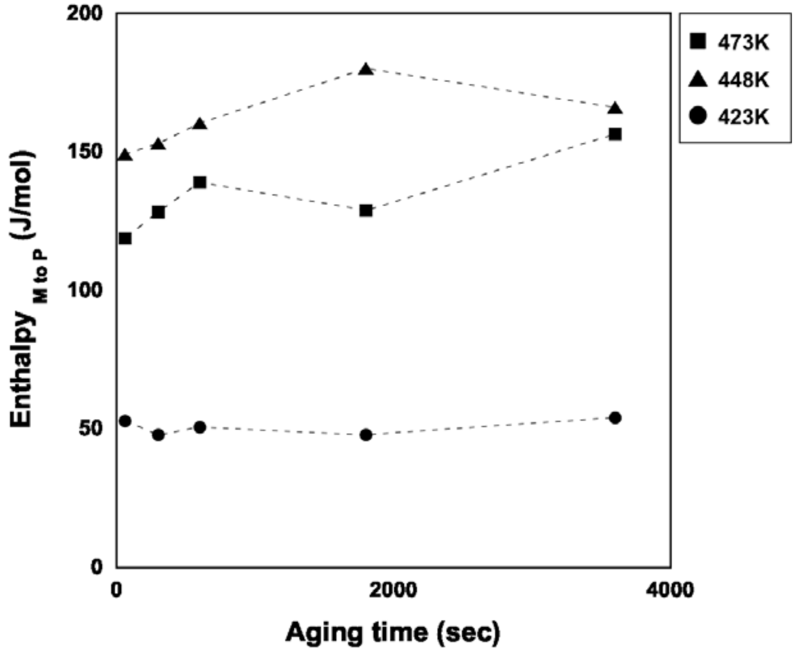

Fig.4. Change in enthalpy of reverse transformation with aging in $Cu_{71}Al_{17}Mn_{12}$ alloy aged at 423K(●), 448K(▲) and

transformation in this alloy depends on aging temperature rather than aging time. This result suggests that aging temperature rather than aging time is important to provide the large enthalpy.

4. Summary

We have investigated effect of aging on the martensitic transformation behaviour in $Cu_{83-X}Al_{17}Mn_X$ alloys by ER and DSC measurements. The results can be summarized as follows:

1) In electrical resistivity measurements, martensitic transformation was clearly observed in aged Cu-Al-Mn alloys including 10 and 12at% of Mn. On the other hands, in the alloys with over 14at% Mn, there are no transformations in the aging condition (373K for 0.6ks).
2) DSC measurements in $Cu_{71}Al_{17}Mn_{12}$ show that the reverse transformation temperatures increase with aging time and reaches to approximately 200K, which is independent of aging temperature.
3) The measured enthalpy of reverse transformation strongly depends on the aging temperature and that slightly increases with the aging time.

A part of this study is financially supported by Graint-in-Aid for Scientific Research on Priority Areas "Next Generation Actuators Leading Breakthroughs" from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] T. Tadaki, *Shape memory materials* (CAMBRIDGE UNIVERSITY PRESS, UK, 1998), p.97.
[2] S. Miyazaki and K. Otsuka, ISIJ Int., **29**, 353 (1989)
[3] R. Kainuma, S. Takahashi and K. Ishida, Metall. Mater. Trans. A, **27A**, 2187 (1996)
[4] Y. Sutou, R. Kainuma and K. Ishida, Mater. Sci. Eng. A., **273-275**, 375 (1999)
[5] Y. Sutou, T. Omori, K. Yamauchi, N. Ono, R. Kainuma and K. Ishida, Acta Mater., **53**, 4121 (2005)
[6] Y. Sutou, T. Omori, A. Furukawa, Y. Takahashi, R. Kainuma, K. Yamauchi, S. Yamashita and K. Ishida, J. Biomed. Mater. Res. Part B; Appl. Biomater., **69B**, 64 (2003)
[7] M. O. Prado, Scripta Mater., **38**, 375 (1993)
[8] M. S. Choi, T. Fukuda and T. Kakeshita, Scripta Mater., **53**, 869 (2005)
[9] K. Tsuchiya, D. Miyoshi, K. Tateyama, K. Takezawa and K. Marukawa, Scripta Metall. Mater., **31**, 455 (1994)
[10] K. Marukawa and K. Tsuchiya, Scripta Metall. Mater., **32**, 77 (1995)
[11] A. Planes, J. L. Macqueron, M. Morin and G. Guenin, Phys. Stat. Sol. (a), **66**, 717 (1981)
[12] J. Van Humbeeck, D. Van Hulle, L. Delaey, J. Ortin, C. Segui and V. Torra, Trans. JIM., **28**, 383 (1987)