Materials Transactions, Vol. 52, No. 8 (2011) pp. 1713 to 1715

EXPRESS RAPID PUBLICATION

Superelasticity at Low Temperatures in Cu-17Al-15Mn (at%) Shape Memory Alloy

Kodai Niitsu*, Toshihiro Omori and Ryosuke Kainuma

Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

Superelasticity at temperatures between 77 K and 273 K in Cu-17Al-15Mn alloy was investigated. In this alloy, where no thermally-induced martensitic transformation appears, an excellent superelasticity with recovery strain of 8.5% was confirmed at 77 K. The critical stresses for stress-induced martensitic transformation decrease with decreasing temperature and its gradient becomes smaller at low temperatures due to the decrease of entropy change. The entropy change estimated at 77 K is −0.46 J/(mol·K), which is almost one-third of that at 221 K.
[doi:10.2320/matertrans.M2011128]

(Received April 25, 2011; Accepted May 23, 2011; Published July 13, 2011)

Keywords: *martensitic phase transformation, shape memory alloy, copper alloys, heusler phases, superelasticity*

1. Introduction

Conventional Ni-Ti shape memory alloys (SMAs) are widely used for various industrial and medical applications such as guide wires because of their excellent shape memory properties, good mechanical properties and corrosion resistance. However, the operation of superelasticity (SE) in practical Ni-Ti alloys is limited in a narrow temperature range near room temperature[1] due to the limitation of the range of martensitic transformation temperature. Although high-temperature SMAs have been extensively investigated,[2,3] shape memory properties at low temperatures potentially needed in cryogenic technologies has been less investigated. In the Ni-rich Ni-Ti alloy system, it is known that the transformation temperature decreases with increasing Ni composition.[4] However, it is difficult to lower the transformation temperature even for high Ni contents because the temperature easily increases due to the precipitation during aging for shape setting.[4] Although SE at 77 K has been reported in Ni-Ti-Fe ternary alloy at 77 K,[5] low temperature SE has not been widely applied for practical use up to now.

Cu-based SMAs such as Cu-Al-Ni and Cu-Zn-Al have the advantage of potential lower costs. It is easy to decrease the martensitic transformation temperature by choosing a suitable alloy composition, and the SE at 77 K has been reported in Cu-Al-Ni alloy.[6] One of the fatal problems of conventional polycrystalline Cu-based alloys, however, is their brittleness. The present authors' group has found that Cu-Al-Mn SMAs offer high ductility of more than 60% in reduction,[7,8] making them attractive for practical applications due to microstructural control.[9–11] Indeed, the Cu-Al-Mn alloys have begun to be used in the medical field.[12] It has recently been reported that Cu-17Al-12Mn (at%) alloy has a martensitic transformation starting temperature M_s of 117 K and that no thermally-induced martensitic transformation takes place in Cu-17Al-14, 16 and 18Mn (at%) alloys.[13] It has been also reported that Cu-18.4Al-12.2Mn (at%) alloy deformed at 77 K exhibits shape memory effect when heated to 293 K with 7% shape recovery.[14] However, there has been no report on SE at cryogenic temperatures in Cu-Al-Mn alloys. In this study, a superelastic tensile test was conducted in the temperature range between 77 K and 273 K in a ductile Cu-Al-Mn alloy.

*Graduate Student, Tohoku University

2. Experiments

A Cu-17Al-15Mn (at%) alloy was prepared by induction melting under an argon atmosphere. The obtained ingot was homogenized at 1173 K for 1 day and annealed at 873 K for 6 h in the α (fcc) and β (bcc) two-phase region, followed by cold swaging to 4 mm in diameter with intermediate annealing at 873 K. The rod specimen was solution-treated at 1173 K for 1 h followed by water quenching and subsequently aged at 473 K for 15 min to stabilize martensitic transformation temperatures. The SE was investigated by a tensile test for one specimen with a gauge length of 16 mm and a diameter of 2 mm containing four coarse grains. The tensile test was conducted at various temperatures in the following order, 77, 127, 177, 227 and 273 K, and finally fractured at 77 K. The fracture surface was observed by scanning electron microscopy (SEM) and thermomagnetic measurement was conducted in the temperature range 6–273 K by superconducting quantum interference device (SQUID).

3. Results and Discussion

Figure 1(a) shows the stress-strain curves at the initial stage of the SE at various temperatures in Cu-17Al-15Mn (at%) alloy. While the plastic strain is observed at 273 K, stress-induced transformation (SIT) and SE are obtained at the temperatures ranging from 77 K and 223 K. The critical stress of SIT (σ_c) increases with increasing temperature. Figure 1(b) shows the whole cycles of stress-strain curves finally tested at 77 K. It is found that this alloy exhibits an excellent SE with perfect shape recovery at 77 K, where the recovery strain of 8.5% including the elastic strains of the parent and martensite phases is obtained. The fracture elongation (ε_f) and ultimate tensile strength (σ_{UTS}) are 7.8% and 504 MPa, respectively. It was confirmed by

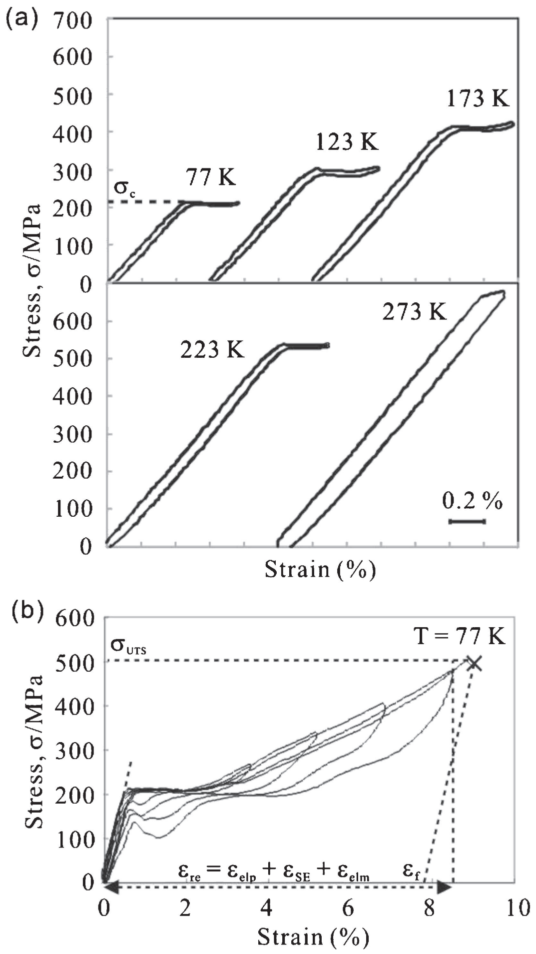

Fig. 1 (a) Stress-strain curves of Cu-17Al-15Mn (at%) alloy in the temperature range 77 K–273 K. Superelasticity is obtained at temperatures lower than 223 K. (b) Cyclic stress-strain curves tested at 77 K for the same specimen as Fig. 1(a). Recovery strain ($\varepsilon_{re} = \varepsilon_{elp} + \varepsilon_{SE} + \varepsilon_{elm}$), fracture elongation ($\varepsilon_f$) and ultimate tensile strength (σ_{UTS}) are 8.5%, 7.8% and 504 MPa, respectively, where ε_{elp}, ε_{SE}, and ε_{elm} are elastic strain of parent phase, superelastic strain and elastic strain of martensite phase.

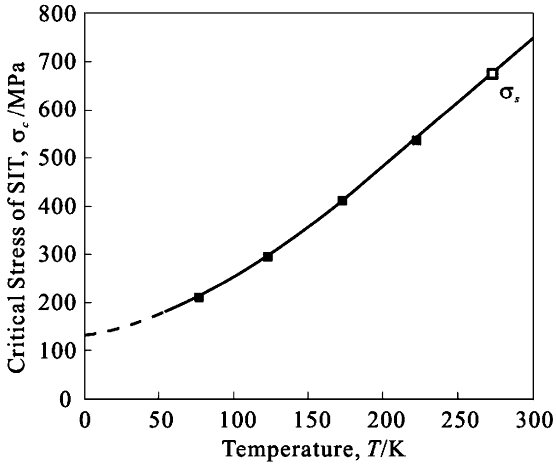

Fig. 2 Temperature dependence of critical stresses obtained in Fig. 1(a). Solid squires are critical stresses for inducing martensite (σ_c) and an open squire at 273 K is critical slip stress (σ_s).

thermomagnetic measurement that this alloy undergoes no thermally-induced martensitic transformation. It is interesting to note that the alloy with no thermal transformation shows stress-induced martensitic transformation in such a large temperature range. In Fig. 1(b), the stress starts to increase at a strain of about 2%. The reason for this behavior is not clear, but it is probably due to formation of other martensite variants in some different grains and the elastic deformation of the stress-induced martensite.

The σ_c defined in Fig. 1(a) are plotted with solid squares in Fig. 2 as a function of the test temperature, where the open square at 273 K indicates the critical stress for slip deformation (σ_s). The σ_c decreases with decreasing temperature, and its slope gradually becomes smaller at low temperatures. It is interesting to note that the σ_s at 273 K is 680 MPa, that is located just on the curve of σ_c extrapolated from the lower temperatures. This suggests that the slip may be induced by the SIT. The relation between the σ_c and temperature (T) is given by the Clausius-Clapeyron equation:

$$\frac{\partial \sigma_c}{\partial T} = -\frac{\Delta S}{\varepsilon \cdot V}, \tag{1}$$

where ΔS, ε and V are the molar entropy difference between the parent and martensite phases, the strain caused by the phase transformation and the molar volume, respectively. This equation means that the $\partial\sigma_c/\partial T$ is proportional to the ΔS because the temperature dependence of the ε is ignorable.[15] It is difficult to obtain the ε value in this study. Therefore, in order to estimate the ε, we use the values of ΔS ($= -1.31$ J/(mol·K)) at 221 K in the Cu-17Al-11Mn (at%) alloy[16] and V ($= 7.59 \times 10^{-6}$ m^3/mol) in the Cu-17Al-10Mn (at%) alloy.[17] If the compositional dependence of ΔS is negligibly small and the ΔS at 221 K in the present alloy is the same as that in the Cu-17Al-11Mn (at%) alloy, the ε is estimated by eq. (1) using the experimental value of the $\partial\sigma_c/\partial T = 2.7$ MPa/°C at 221 K in Fig. 2 to be 6.4%, which is smaller than the recovery strain of 8.5% in Fig. 1(b) because the recovery strain includes the elastic strain of the parent and martensite phases. By using this ε, the ΔS, for instance, at 77 K, can be estimated from the experimental data of the $\partial\sigma_c/\partial T$ as being about -0.49 J/(mol·K), which is almost one-third of that at 221 K. Thus, the decrease in the slope of critical stress at low temperatures in Fig. 2 is reasonably explained by the temperature dependence of ΔS, which should decrease with decreasing temperature at very low temperatures and ideally reach zero at 0 K.

Figure 3(a) shows the secondary electron image (SEI) of the fracture surface of the specimen tested at 77 K and Fig. 3(b) exhibits its high magnification image. Almost no reduction of area is observed in this specimen, and the microstructure seen in Fig. 3 suggests that the fracture at 77 K is mainly due to the cleavage mode. This result is coincident with the fact that plastic strain is hardly observed in the tensile test of Fig. 1(b). It has been reported that the Cu-Al-Mn alloy with a coarse grain structure shows ductile fracture with large reduction of area and dimple pattern at room temperature,[18] and therefore, the lower ductility in this study was caused by cold brittleness, as observed in other shape memory alloys with the BCC structure.[19]

In this study, the temperature dependence of SE in a Cu-17Al-15Mn (at%) alloy with a large grain size was investigated in the temperature range 77 K–273 K. This alloy

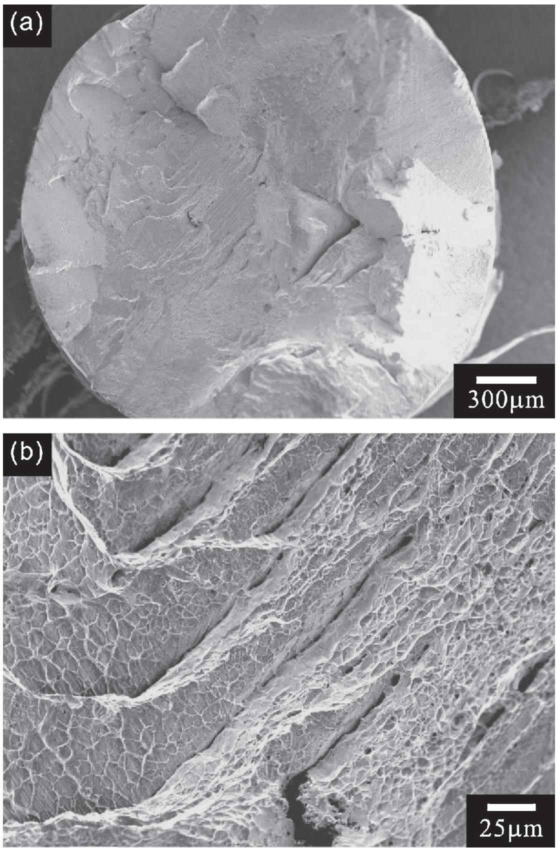

Fig. 3 (a) Secondary electron images (SEIs) of fracture surface of Cu-17Al-15Mn (at%) after tensile test at 77 K shown in Fig. 1(b), and (b) high magnification image.

was found to exhibit the SE at temperatures between 77 K and 223 K, although no thermal martensitic transformation takes place, and a large recovery strain of about 8.5% was obtained at 77 K. The fracture elongation and ultimate tensile strength at 77 K are 7.8% and 504 MPa. The critical stress to induce martensitic transformation decreases with decreasing temperature, the gradient becoming lower at low temperatures, which is reasonably explained by the decrease of the entropy change at low temperatures. The entropy change at 77 K is estimated as being about $-0.46\,\mathrm{J/(mol \cdot K)}$ using the Clausius-Clapeyron equation.

Acknowledgement

This study was supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) and by the Global COE Program.

REFERENCES

1) P. G. Lingquist and C. M. Wayman: *Engineering Aspects of Shape Memory Alloys*, ed. T. W. Duerig, K. N. Melton, D. Stockel and C. M. Wayman, (Butterworth-Heinemann, London, 1990) p. 58.
2) J. Van Humbeeck: J. Eng. Mater. Tech. **121** (1999) 98.
3) G. S. Firstov, J. Van Humbeeck and Y. N. Koval: Mat. Sci. Eng. A **378** (2004) 2.
4) K. Otsuka and X. Ren: Prog. Mater. Sci. **50** (2005) 511.
5) T. W. Duerig and R. Zadno: *Engineering Aspects of Shape Memory Alloys*, ed. T. W. Duerig, K. N. Melton, D. Stockel and C. M. Wayman, (Butterworth-Heinemann, London, 1990) p. 369.
6) V. I. Nikolaev, S. A. Pul'nev, G. A. Malygin, V. V. Shpeizman and S. P. Nikanorov: Phys. Solid State. **49** (2007) 1878.
7) R. Kainuma, S. Takahashi and K. Ishida: J. Phys. IV **5** (1995) 961.
8) R. Kainuma, S. Takahashi and K. Ishida: Metall. Mater. Trans. A **27A** (1996) 2187.
9) Y. Sutou, T. Omori, R. Kainuma, N. Ono and K. Ishida: Metall. Mater. Trans. A **33A** (2002) 2817.
10) Y. Sutou, T. Omori, K. Yamauchi, N. Ono, R. Kainuma and K. Ishida: Acta Mater. **53** (2005) 4121.
11) Y. Sutou, T. Omori, R. Kainuma and K. Ishida: Mater. Sci. Tech. **24** (2008) 896.
12) M. Ishibashi, N. Tabata, T. Suetake, T. Omori, Y. Sutou, R. Kainuma, K. Yamauchi and K. Ishida: J. Dermatol. Treat. **19** (2008) 291.
13) S. Ii, K. Tsuchiya and T. Koyano: Proc. 8th European Symposium on Martensitic Transformation (ESOMAT 2009), (2009) p. 02011.
14) G. Zak, A. C. Kneissl and G. Zatulskij: Scr. Mater. **34** (1996) 363.
15) K. Otsuka, H. Sakamoto and K. Shimizu: Acta Metall. **27** (1979) 585.
16) T. Omori, Y. Sutou, N. Tabata, R. Kainuma and K. Ishida: J. Japan Res. Inst. Adv. Copper-Base Mater. Technol. (JRI Cu) **50** (2011) to be published.
17) Y. Sutou, T. Omori, R. Kainuma, N. Ono and K. Ishida: Metall. Mater. Trans. A **33A** (2002) 2817.
18) Y. Araki, T. Endo, T. Omori, Y. Sutou, Y. Koetaka, R. Kainuma and K. Ishida: Earthquake Eng. Struct. Dynam. **40** (2011) 107.
19) P. P. Rodriquez, R. B. Perez-Saez, V. Recarte, J. M. San Juan, O. A. Ruano and M. L. No: REVISTA DE METALURGIA **37** (2001) 194.