Effect of Al Content and Annealing Temperature on Cold Workability of CuAlMn Alloys

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Abstract. The effect of Al content and annealing temperature on the cold workability of CuAlMn alloys has been studied by testing machine, metallographic analysis and XRD method. The study results showed that because of martensite and ductile phase the cold workability of Cu-17.55Al-9.9Mn (at %) alloy was much better than Cu-19.1Al-9.9Mn (at %) alloy. Besides Al content, annealing temperature effects the cold workability of CuAlMn alloys. With the annealing temperature increasing from 525 ℃ to 700 ℃, the cold workability of Cu-17.55Al-9.9Mn (at%) alloy increased gradually and reached 75%. However, the cold workability of Cu-19.1Al-9.9Mn (at %) alloys annealed from 525 ℃ to 700 ℃ was low. Furnace-cooling could be an effective annealing technique to improve the cold workability of Cu-19.1Al-9.9Mn (at %) alloy.

1. Introduction

Shape memory alloys have been studied widely because of their unique shape memory effect, super-elasticity and damping capacity. Among the traditional shape memory alloys, as well known, NiTi alloys show excellent shape memory effect. However, NiTi alloys are expensive. Fe-based alloys are cheap, but their recoverable strains are rather low. Cu-based alloys with good shape memory effect and rather low cost suffered from poor mechanical property. For example, both Cu-Zn-Al alloys and Cu-Al-Ni alloys are poor in ductility due to the large grain size, fragility in grain boundary and high elastic anisotropy [1, 2]. As a result, the wide use of shape memory alloys in engineering areas has been limited.

Studies showed that Cu-Al-Mn alloys with a lower Al content showed excellent ductility because their parent phase with an L21 structure possessesed a low degree of order[3]. The phase stability [4] and the effects of alloying elements [5-8], grain size [9], texture [9,10] and ageing [11,12] on their cold workability and damping capacity as well as shape memory effect have been further investigated [13, 14]. Kainuma etc. have studied the cold workability of Cu-(14~17) Al-10Mn (at%) alloys and found that the alloys show good cold workability[3].

The present samples were obtained by annealing at different temperatures and then cold rolling. It was found that the cold workability was influenced significantly by not only Al content but also the annealing temperature. It was also found that the cold workability of CuAlMn alloy with Al content higher than 19 at% was rather poor but it could be improved through different annealing technique. To our knowledge, no reports are available on the effect of annealing temperatures on the cold workability of CuAlMn shape memory alloys with a lower aluminum and higher manganese content. Therefore, studies on the cold workability of Cu-based alloys might make the application of this potential shape memory alloy possible. The purpose of this paper is to study the effect of Al content and annealing techniques on the cold workability of CuAlMn alloys.

2. Experimental procedures

Two sets of CuAlMn alloys, Cu-17.55Al-9.9Mn and Cu-19.1Al-9.9Mn (at %) designated as 17Al and 19Al respectively, were prepared for the present study. The alloys were prepared by vacuum induction melting, using 99.9wt.% Cu, 99.3wt.% Al, 99.9wt.% Mn. After homogenization at 820℃ for 23 h, the ingots were squeezed into bars of 11 mm diameter at 800 ℃. All cylindrical samples for test were cut from these bars, called original sample. The diameter (d) and the height (h) of the samples were defined according to the engineering standard [15].

All 17Al original samples and some 19Al original samples were annealed at different temperatures from 525 ℃ to 700 ℃ for 30 min, followed by water quenching. The other 19Al original samples were subjected to two different annealing techniques as following: 1) annealed at 800 ℃, 750 ℃, 700 ℃ for 30 min firstly, then furnace-cooled to 400 ℃, called furnace-cooling sample of 19Al; 2) annealed at 400 ℃ for 30 min, called annealing sample of 19Al.

After different heat treatment mentioned above, these samples would undergo cold-working. The cold-working test was carried at WAW-300 testing machine at room temperature and the loading speed is 0.016mm/min. ω was used to denote the cold workability: $\omega=(h_0-h_1)/h_0$, where h_0 is the initial height and h_1 corresponds to the minimum height, before a crack appeared during the test.

The microstructures were examined by S-3400N scanning electronic microscope and OLYMPUS-CK40M optical microscope. The phases present in the samples at room temperature were analyzed by X-ray diffraction using Cu-Kα radiation with Philips XPert PMD.

3. Result

Figure1 shows the cold workability of 17Al and 19Al samples annealed at different temperatures. The cold workability ω of 17Al sample annealed at 525 ℃ was about 25%, a little lower than that of 17Al originl sample, which was about 30%. It is seen from Figure1 that ω increased slowly at first and then steeply for the sample annealed at 650 ℃, up to about 75% for the sample annealed at 700 ℃. On the other hand, ω of 19Al samples annealed from 525 ℃ to700 ℃ was about 15%~20%, similar to that of 19Al original sample. Noticed that the cold workability of 17Al sample annealed at 700 ℃ was much higher than 19Al sample annealed at 700 ℃.

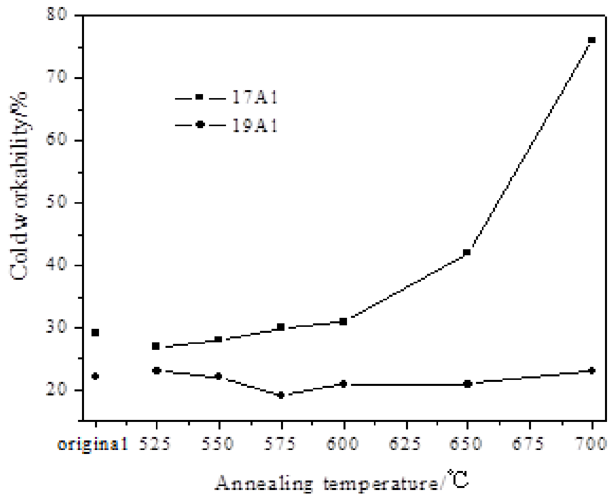

Figure 1. Effect of annealing temperatures on the cold workability of 17Al and 19Al samples

Figure 2 is the microstructures of 17Al samples. Noticed that there was much blocky phase in the original sample. The sample annealed at 525 ℃ contained blocky phase and banding phase. With the annealing temperature increasing to 650 ℃, the sample contained more banding phase and less blocky phase.

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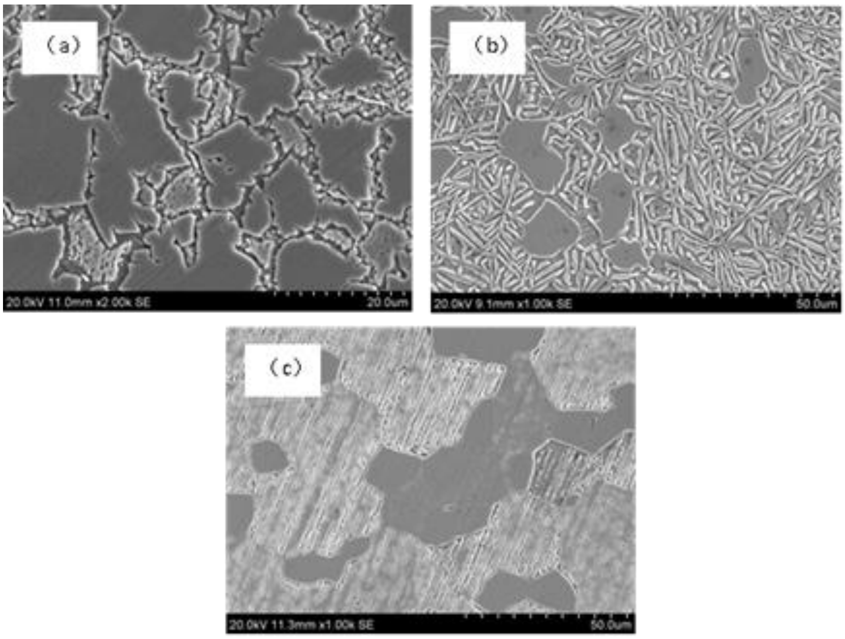

Figure 2. SEM images of 17Al samples: a) original, b) annealed at 525 ℃, c) annealed at 650 ℃.

Figure 3 is XRD patterns of 17Al samples annealed at 700 ℃. It is seen that the 17Al sample annealed at 700 ℃ before cold-working contained much $L2_1\beta$ parent phase while the sample after cold-working contained much 18R martensite, which is stress-induced martensite.

Figure 4 is the stress-strain curves of 17Al samples annealed at 525 ℃ and 700 ℃ respectively. With the stress increasing, the strain of the sample annealed at 700 ℃ increased linearly mainly at first. Then the curve droped from point B with the increase of the stress and the slope coefficient increased generally, as shown in the imaginary line. On the other hand, the strain of the sample annealed at 525 ℃ increased linearly too at first, as shown in real line section from origin to point A. With the stress increasing, the slope coeffecient fell down until the sample fractured. It indicated that 17Al samples annealed at 700 ℃ have better ductility.

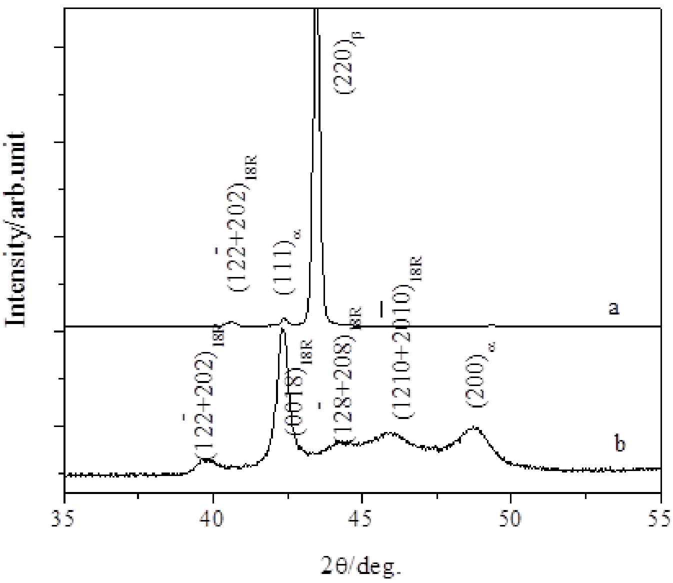

Figure 3. XRD patterns of 17Al samples: a) annealed at 700 ℃, b) annealed at 700 ℃ and cold-worked

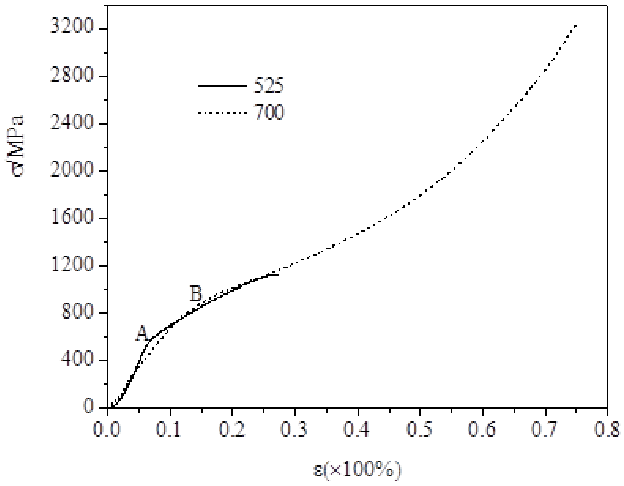

Figure 4. Stress-strain curves of 17Al samples annealed at 525 ℃ and 700 ℃ respectively

Figure 5 shows the microstructures of 19Al samples. Noticed that much banding phase was introduced after cold-working in the samples annealed at 525 ℃ and 700 ℃, as well as the original samples.

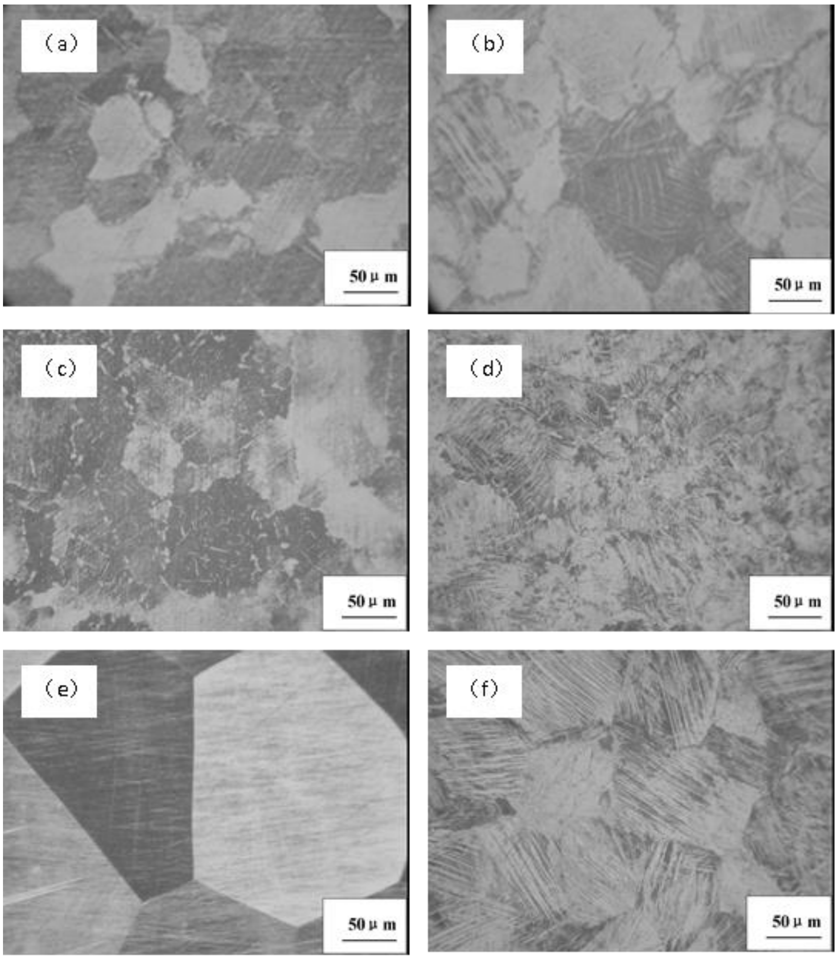

Figure 5. Optical micrographs of 19Al alloys a) original, b) original and cold-worked, c) annealed at 525 ℃, d) annealed at 525 ℃ and cold-worked, e) annealed at 700 ℃, f) annealed at 700 ℃ and cold-worked.

Figure 6 is vertical section in 10 at% Mn of phase equilibria of Cu-Al-Mn syetem[3].

Figure 7 is the XRD patterns of the cold-worked 17Al and 19Al samples annealed at 700 ℃. After cold-working there was much 18R martensite in 17Al sample, along with a little β_1 parent phase and α-phase. While in 19Al sample there was no other phase but martensite. Noticed that the $(1\ 1\ 1)_{18R}$ and $(0\ \bar{1}\ 9)_{18R}$ martensite diffraction peaks of 19Al sample were much sharper than 17Al. And the $(1\ 2\ \bar{2})_{18R}$ and $(2\ 0\ 2)_{18R}$ martensite diffraction peaks of 19Al sample were separate.

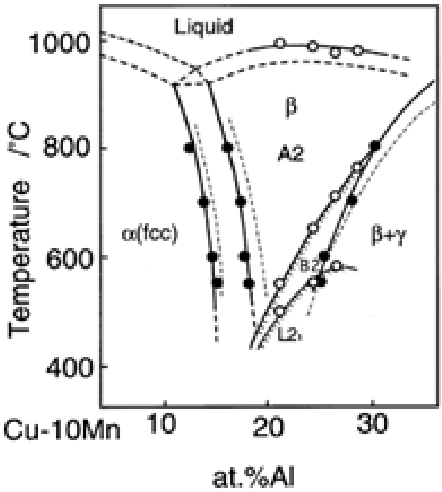

Figure 6. Vertical section in 10 at% Mn of phase equilibria of Cu-Al-Mnsyetem [3]

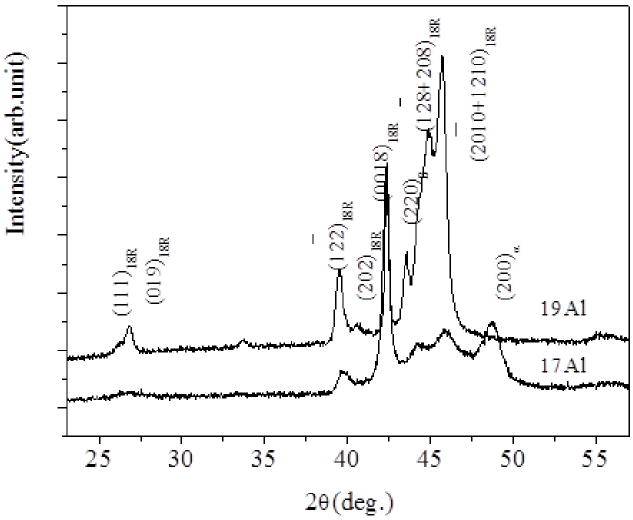

Figure 7. XRD patterns from 17Al and 19Al samples annealed at 700 ℃ and cold-worked

Figure 8 is the cold workability of 19Al samples subjected to two different annealing techniques. It is seen the cold workability of the furnace-cooling samples was nearly 30%, much higher than that of the annealing sample, which was only 14%.

Figure 9 is the microstructures of 19Al samples subjected to two different annealing techniques. There was much banding phase and little particle phase in the annealing sample of 19Al. While in the furnace-cooling sample of 19Al there was much blocky phase.

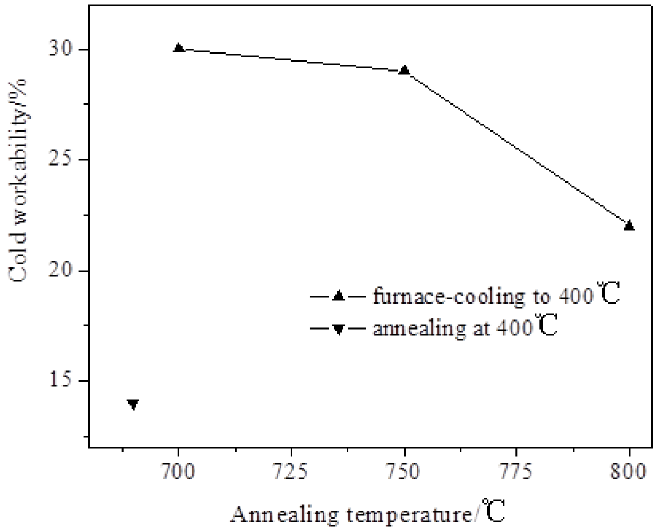

Figure 8. Cold workability of the furnace-cooling sample and annealing sample of 19Al, respectively

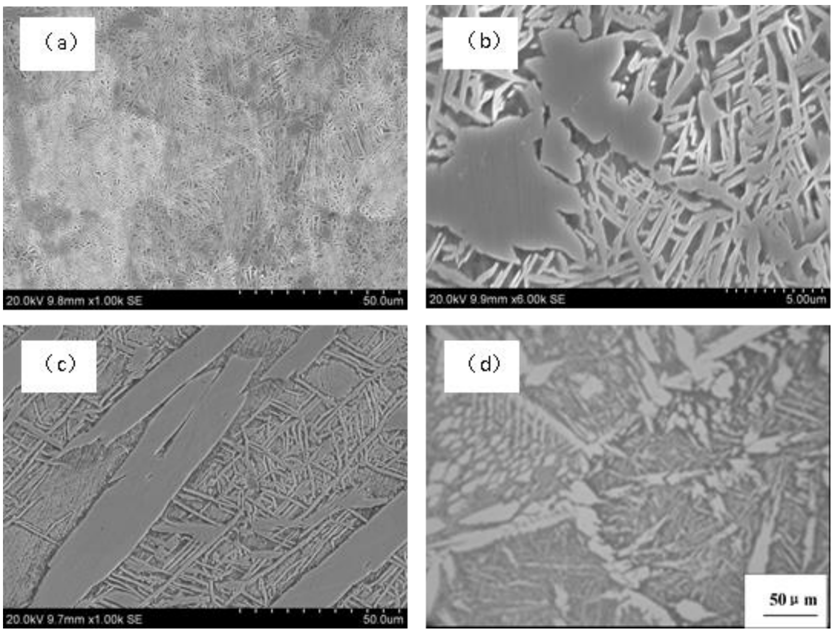

Figure 9. SEM and OM images of 19Al samples: a, b) annealed at 400 ℃, c) annealed at 800 ℃ and furnace-cooled to 400 ℃, d) annealed at 700 ℃ and furnace-cooled to 400 ℃

4. Discussion

The cold workability of 17Al sample annealed at 525 ℃ was about 25%, as shown in Figure1, a little lower than that of the original sample, which contained much ductile blocky phase, as shown in Figure 2(a). The reason might be γ-phase precipitation from β-phase when the sample was annealed at 525 ℃. With the annealing temperatures increasing, α-phase and γ-phase melted grandually into β-phase. Because of the disappearance of the brittle γ-phase, the cold workability of the sample annealed at 650 ℃ increased sharply. The cold workability of the sample annealed at 700 ℃ was above 75%, much better than that of 525 ℃. The reason might be stress-induced martensite transformation because there was much martensite introduced in the cold-worked sample, as shown in Figure 3.

When the sample annealed at 700 ℃ was subjected to stress, the parent phase deformed elasticly at first and then, with the stress increasing, the slope coefficient decreased, which indicated stress-induced martensite transformation from the parent phase, as shown in the imaginary line in Figure 4.

Subsequently, the slope coefficient increased, which indicated the elastic deformation and reorientation in stress-induced martensite [16]. Since stress-induced martensite transformation preceded continiously, the cold workability of 17Al sample annealed at 700 ℃ increased remarkably. It indicated that for CuAlMn alloy with lower Al content stress-induced martensite transformation could improve the cold workability remarkably.

Different from 17Al alloy, the cold workability of 19Al alloy with higher Al content was relatively low, as shown in Figure1. Because of high Al content, 19Al alloy was basically in single β-phase at high temperature, according to CuAlMn phase diagram [1]. When 19Al samples were subjected to stress, stress-induced martensite was introduced, as shown in Figure5. However, the cold workability of them kept low.

As is known, at high temperature CuAlMn alloy has disorder bcc structure, called A2. When quenched, it undergoes disorder-order transitions, according to the reaction sequence as $A2 \rightarrow B2 \rightarrow L2_1$ [1], as shown in Figure6. With Al content increasing, the disorder-order transition temperatures increase and accordingly the A2 region reduces. So with Al content increasing, the alloy tends to have parent phase or martensite with high degree of order. As is known, plastic deformation occurs through dislocation glide. The easier the dislocation glides, the better plasticity the alloy has [17]. The dislocation moves more difficultly in parent phase or martensite with higher degree of order in Cu-based shape memory alloys [2, 18].

The degree of order of Cu-based shape memory alloy could be denoted by several methods. The intensity of (1 1 1) and (0 1 9) superlattice diffraction peaks and the spacing differences (△ d) between some selected pairs of martensite diffraction planes reflect the degree of order of $L2_1$ parent phase or martensite [1, 19, 20]. So according to its sharp (1 1 1) and (0 1 9) peaks and the separated (1 2 $\bar{2}$) and (2 0 2) peaks, as shown in Figure7, 19Al sample could be considered to possess higher degree of order than 17Al. That might be one of the reasons why its plasticity was poorer than 17Al. Another reason might be the lack of ductile α-phase after annealing.

However, the cold workability of 19Al sample annealed at 700 ℃ and furnace-cooled to 400 ℃ was about 30%, as shown in Figure8, much higher than that of the sample annealed at 400 ℃. The reason might be the ductile α-phase precipitation during furnace-cooling from high temperature, as shown in Figure 9(c) and (d). This result indicated that for CuAlMn alloy with higher Al content, furnace-cooling might be an effective heat treatment technique to improve the cold workability.

5. Conclusions

1) The 17Al alloy annealed at 700 ℃ showed excellent cold workability, up to 75%. The cold workability caused by stress-induced martensite transformation is much better than that caused by ductile α-phase.

2) The cold workability of 19Al alloy keeps lower than that of 17Al alloy. The high degree of order and lack of ductile α-phase after annealing might be the reasons. Furnace-cooling is an effective heat treatment technique to improve the cold workability of CuAlMn alloy with high Al content.

6. References

[1] XU Zuyao. Shape Memory Materials. ShangHai:Shang Hai JiaoTong University Press. 2000. (in Chinese)
[2] Zhao Lian-cheng, Cai Wei, Zheng Yu-feng. Shape Memory Effect and Superelasticity in Alloys. BeiJing: National Defence Industry Press. 2002. (in Chinese)
[3] R.Kainuma,S.Takahashi,K.Ishida. Thermoelastic martensite and shape memory effect in ductile Cu-Al-Mn alloys [J] .Metal. Mater. Trans.1996, 27: 2187-2195.
[4] R. Kainuma, N. Satoh , X. J. Liu, I. Ohnuma, K. Ishida. Phase equilibria and Heusler phase stability in the Cu-rich portion of the Cu–Al–Mn system[J]. J. Alloys Compd. 266 (1998) 191-200.
[5] Y.Sutou, R.Kainuma, K.Ishida. Effect of alloying elements on the shape memory properties of ductile Cu-Al-Mn alloys [J]. Mater. Sci. Eng. A 273-275 (1999) 375-379.
[6] U.S. Mallik, V. Sampath, Effect of alloying on microstructure and shape memory characteristics of Cu-Al-Mn shape memory alloys[J]. Mater. Sci. Eng. A 481-482 (2008) 680-683.

[7] U.S. Mallik, V. Sampath. Influence of quaternary alloying additions on transformation temperatures and shape memory properties of Cu-Al-Mn shape memory alloy [J]. J. Alloys Compd. 459 (2009) 156-163.
[8] U.S.Mallik, V.Sampath. Influence of aluminum and managanese concentration on the shape memory characteristics of Cu-Al-Mn shape memory alloys [J]. J. Alloys Compd. 459 (2008) 142-147.
[9] Y. Sutou, T. Omori, K. Yamauchi, N. Ono, R. Kainuma, K.Ishida. Effect of grain size and texture on pseudoelasticity in Cu-Al-Mn-based shape memory wire [J]. Acta Mater. 53 (2005) 4121–4133.
[10] Y. Sutou, T. Omori, R. Kainuma, N. Ono and K. Ishida. Enhancement of Superelasticity in Cu-Al-Mn-Ni Shape Memory Alloys by Texture Control [J]. Metall. Mater. Trans. A, 33 (2002) 2817–2824.
[11] Y.Sutou, T.Omori, N.Koeda, R.Kainuma, K.Ishida. Effects of grain size and texture on damping properties of Cu-Al-Mn-based shape memory alloys[J]. Materials Science and Engineering A 438–440 (2006) 743–746.
[12] Q.Z. Wang, D.M. Lu, C.X. Cui, W.J. Liu, M. Xu, J. Yang. Effects of aging on the structure and damping behaviors of a novel porous CuAlMn shape memory alloy fabricated by sintering–dissolution method. Materials Science & Engineering A, 615 (2014) 278–282.
[13] J.P. Oliveira, Z. Zeng, T. Omori, N. Zhou, R.M. Miranda, F.M. Braz Fernandes. Improvement of damping properties in laser processed superelastic Cu-Al-Mn shape memory alloys. Materials and Design 98 (2016) 280–284.
[14] Y.Q. Jiao, Y.H. Wen, N. Li, J.Q. He, J. Teng. Effect of solution treatment on damping capacity and shape memory effect of a CuAlMn alloy. Journal of Alloys and Compounds 491 (2010) 627–630.
[15] GB/T 7314-2005, Metallic materials-Compression testing at ambient temperature. BeiJing: Standards Press of China, 2005.
[16] XU Zuyao. Martensite Transformation and Martensite. Beijing:Science Press.1999. (in Chinese)
[17] Hu-gengxiang. Fundamentals of Materials Science. ShangHai:ShangHai JiaoTong University Press. 2001. (in Chinese)
[18] Zhou Jiubao, Xi Kang. Shape Memory Alloy. Beijing: Machanical Engieering Press. 1984. (in Chinese)
[19] M. Eskil, N. Kayali. X-ray analysis of some shape memory CuZnAl alloys due to the cooling rate effect[J]. Mate. Lett. 60 (2006) 630-634.
[20] A. Aydogdu, Y. Aydogdu, O. Adiguzel. Long-term ageing behaviour of martensite in shape memory Cu-Al-Ni alloys[J]. Journal of Materials Processing Technology. 153-154 (2004) 164-169.