LETTER

# Effect of aging on transformation behavior and shape memory effect of a CuAlNb high temperature shape memory alloy

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Recently, considerable interests have been focus on the possibility of commercial producing shape memory alloys with a relative high martensitic transformation temperature (i.e. above 473 K) and excellent shape memory effect. The candidates for these shape memory alloys include Cu-based system and TiNi-X (X = Pd, Pt, Zr, Hf) alloy [1]. TiNi-X alloys are very expensive owing to the addition of third noble element, and their commercial applications have been greatly limited [2, 3]. CuAlNb alloy is a kind of newly developed shape memory alloys exhibiting the similar properties like CuAlNi alloy. The addition of Nb is effective in reducing the grain size and creating the precipitates, resulting in the increase of mechanical properties and plasticity. Thus, the morphology and the amount of precipitated second phase have obvious effects on the martensitic transformation and mechanical behavior of CuAlNb alloys. Though there is a substantial amount of work devoting to the effect of the Nb content on the precipitated phase and mechanical behavior [4–10], little effort have been carried out on the aging behavior of the CuAlNb alloys. The aim of the present work is to investigate the effect of aging on transformation behavior and shape memory effect for the CuAlNb alloy by DSC measurements and bending tests at different temperatures.

The $Cu_{72}Al_{26.5}Nb_{1.5}$ alloy was prepared by consumable arc melting of metal element Cu, Al, Nb with a purity of 99.99% in an argon atmosphere. The ingot was re-melted five times for chemical homogenization. After solid solution treated at 1173 K for 12 h, the ingot was hot rolled at 1123 K to the thickness of 2 mm, and the samples were cut by a spark cutting machine from the plate, then solution-treated at 1123 K for 30 min followed by quenching into the ice salt-water. Subsequently, the samples were individually aged at 573 and 673 K for various times in a vacuum-sealed silica tube with a vacuum of $10^4$ Torr.

The effect of aging on transformation temperatures was measured by differential scanning calorimeter (DSC), which was carried out from 373 to 723 K using Perkins–Elmer DSC-7 with a heating or cooling rate of 15 K/min. The transformation temperatures were determined as the points where the peaks started to deviate from the baseline, and the transformation temperatures of solution-treated sample were determined as follows: $M_s$ = 558 K, $M_f$ = 552 K, $A_s$ = 586 K, $A_f$ = 632 K.

The shape memory effect (SME) was examined by bending testing at different temperatures using the plate specimens of dimensions of $55 \times 1 \times 0.4$ mm, as shown in Fig. 1. One end of the strip sample was clipped at the center of the plate. The specimen was bent at different temperature, and then heated up to the temperature above $A_f$ temperature. The deform strain was determined by $\varepsilon_t = h/(d + h)$, and the deformation strain used in the present study is 2%. The recovery ratio ($\eta$) was calculated as the following equation: $\eta = (\theta_d - \theta_h)/\theta_d$.

Figure 2 shows the effect of aging time on the martensitic reverse transformation temperatures for specimen aged at 573 K (in the martensitic state). It can be seen that the martensite reverse transformation temperatures, namely $A_S$ and $A_f$, increase with the

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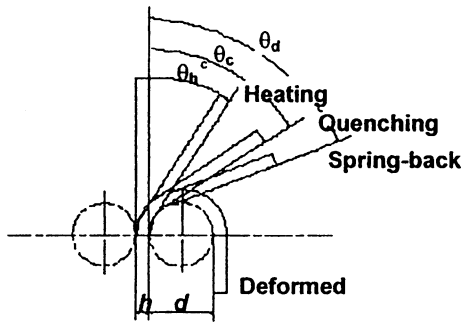Institute of Technology, Harbin 150001, China
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**Fig. 1** Schematic diagram of shape memory effect measurement in the bending test

increasing of the aging time, and the curves can be divided into two stages. In the initial stage of aging (aging time less than 5 h), $A_s$ and $A_f$ increase rapidly with the aging time increasing. When the aging time exceeds 5 h, $A_s$ and $A_f$ increase slowly with an increase of aging time. As $A_s$ and $A_f$ increase with aging time increasing, it is reasonable to believe that the martensitic reverse transformation is suppressed by the aging treatment, termed "stabilization of martensite." When Cu-based shape memory alloys aged in the martensite phase, the concentration of the quenched-in vacancies induces the pinning effect of the interfaces between parent and martensite and between martensite variants, which may be the cause of the "stabilization of martensite."

Figure 3 shows the effect of aging time on the transformation temperatures when the experimental alloy aged at 673 K (in parent state). It can be seen that the martensitic transformation temperature and its reverse transformation temperature show different tendency with the increasing of aging time. The martensitic transformation peak temperature drops with an increase of aging time in the initial stage of aging and keep constant with the further increasing of time,
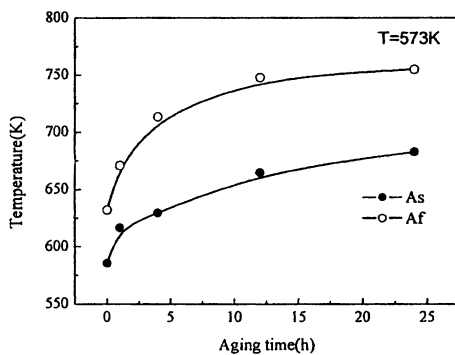
which may be the results of the coherence strain field and/or the destruction of potential nucleation sites of martensites due to the precipitation of $\gamma_2$ phase.

However, the reverse martensitic transformation peak temperature $A_p$ shows different behavior during the aging in the parent phase. From Fig. 3, we can see that the $A_p$ increases in the early stage of aging and keeps stable with the further increase of aging time. It is well known that the precipitation of equilibrium $\gamma_2$ phase takes place when Cu-based shape memory alloy is aged in the parent phase. With the precipitation and growth of $\gamma_2$ phase, the Al content in the matrix is depleted, resulting on the increasing of the $A_p$ temperature.

The martensitic transformations from metastable parent to martensitic phase are essential for the occurrence of shape memory effect. As the aging treatment has greatly influenced the martensitic transformation behavior, it is natural that the SME is more or less subject to aging effects in both phases. Thus two aging treatments were also carried out on the sample: the first was an aging at 573 K for various time followed by ice salt-water quenched and the second was an aging at 673 K for various time and finally ice salt-water quenched.

Figure 4 shows the variation of shape recovery ratio with the aging time for the specimen aged at 573 K. It can be seen that the shape recovery ratio decreases rapidly with increasing aging time in the initial stage of aging treatment and then does not change with increasing the aging time.

Figure 5 also depicts the effect of aging time on the shape recovery ratio for the specimen aged at 673 K. Clearly, the shape recovery ratio decreases almost linearly with the prolongation of the aging time in the first stage of aging. When the aging time exceeds 4 h, the shape recovery ratio become stable and the value is almost 50%.
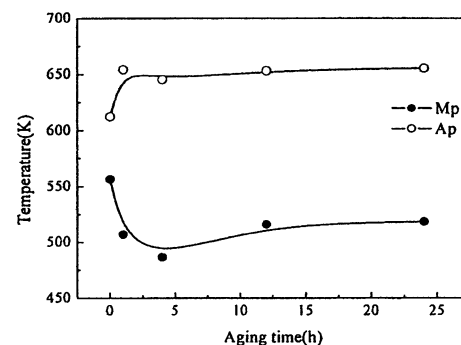


**Fig. 2** Effect of aging time on reverse martensitic transformation temperatures for $Cu_{72}AlL_{26.5}Nb_{1.5}$ alloy aged at 573 K aging time (h)



**Fig. 3** Effect of aging time on transformation temperatures for $Cu_{72}Al_{26.5}Nb_{1.5}$ alloy aged at 673 K

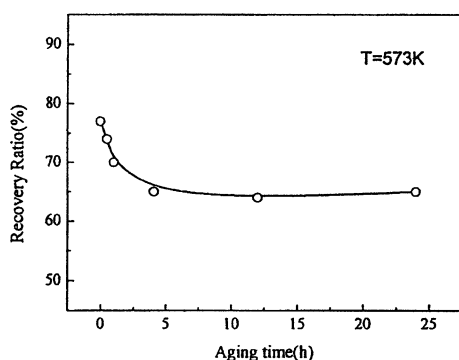**Fig. 4** Variation of shape recovery ratio with the aging time for the specimen aged at 573 K
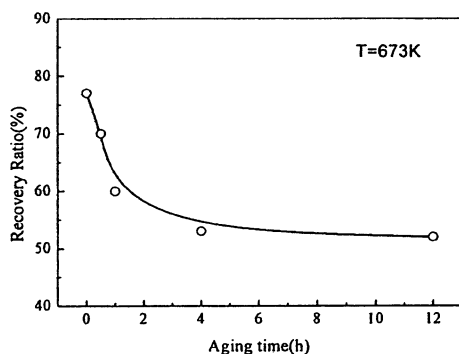


**Fig. 5** Variation of shape recovery ratio with the aging time for the specimen aged at 673 K

In summary, the effect of aging on transformation behavior and shape memory effect of the CuAlNb high temperature shape memory alloy is as follows:

(1) $Cu_{72}Al_{26.5}Nb_{1.5}$ alloy shows a pronounced martensitic stabilization. The reverse martensitic transformation temperatures of $Cu_{72}Al_{26.5}Nb_{1.5}$ alloy aged in the martensitic state increase remarkably with the increase of aging time.

(2) For the $Cu_{72}Al_{26.5}Nb_{1.5}$ alloy aged in the parent phase, its martensitic transformation temperature drops at first, then becomes stable with the increasing aging time. Whereas the reverse martensitic transformation temperature increases with an increase of the aging time in the initial stage, then keeps constant with the further increasing of the time.

(3) The recovery ratio of the aged $Cu_{72}Al_{26.5}Nb_{1.5}$ alloy decreases with the increasing of the aging time in the first stage of aging treatment, then keeps constant with the further increasing of the aging time.

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