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Influence of heat treatment on the transformation hysteresis of CuAlNiMnTi shape-memory alloys

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The electrical resistance method, metallograph analysis, TEM observation and X-ray diffraction analysis have been employed to investigate the influence of heat treatment on the transformation hysteresis ($A_f - M_s$) of CuAlNiMnTi shape-memory alloys (SMAs). It was found that when the quenching specimens were subjected to ageing treatment, the transformation temperature was decreased and the transformation hysteresis was initially increased, but then tended towards stability; when the quenched specimens were subjected to moderate-temperature treatment at 600 °C, the transformation temperature decreased and the amount of transformation also decreased. The type of thermoelastic martensitic transformation changed from type I and type II and then to type I again, and the transformation hysteresis initially decreasing and then increasing, accompanying the change of the type of thermoelastic martensitic transformation. The reason for this lies in the fact that ageing treatment leads to the precipitation of NiAl-based phase, while moderate-temperature treatment leads to the precipitation of α-phase.

1. Introduction
An important feature for thermo-elastic martensite transformation lies in its small transformation hysteresis. It is known from the martensite transformation investigation that the transformation hysteresis of different alloys, which can be determined from the electrical resistance versus temperature curve, is quite different. Because of the complex interaction between the composition elements of CuAlNiMnTi shape-memory alloys (SMAs), the microstructure of this alloy can be changed greatly according to the heat treatment to which it is subjected [1]. Therefore, the type of transformation hysteresis will also be changed. In the present work, the influence of ageing and moderate-temperature treatment on the transformation hysteresis of CuAlNiMnTi SMAs was investigated.

2. Experimental procedure
The alloy with the composition Cu–11.88Al–5.06Ni–1.63Mn–0.96Ti (wt %) was used. The ingots were homogenized at 850 °C for 4 h and then hot-rolled at 850 °C to 2.5 mm slabs. The dimensions of the specimens used for transformation temperature measurement were 2 mm × 2.5 mm × 100 mm. After quenching from 950 °C in 10 min, the specimens were subjected to ageing or moderate-temperature treatment; the ageing temperature was 350 °C and the treatment times were selected as 10 min, 3 h and 4 h, respectively; the moderate-temperature was 600 °C with the holding times were 3, 5, 15, 20 min, respectively. The electrical resistance method was used to measure the transformation temperature. TEM observation was performed using a JEM-100CX II type transmission electron microscope, and X-ray diffraction was performed using XD-3A type X-ray diffraction equipment.

3. Results and discussion
The electrical resistance versus temperature curves for the quenching specimens aged at 350 °C for different times (10 min, 3 h, 4 h) are shown in Fig. 1. It can be seen that as a result of 10 min ageing treatment, the transformation temperature can be severely decreased and the transformation hysteresis can be increased. The transformation temperature shows a slight decrease during further ageing, but the transformation hysteresis remains unchanged.

The electrical resistance versus temperature curves for the quenched specimens followed by moderate-temperature treatment at 600 °C for different times (3, 5, 15, 20 min) are shown in Fig. 2. It can be seen by comparing with Fig. 1 that with increasing holding time, the transformation temperatures decrease

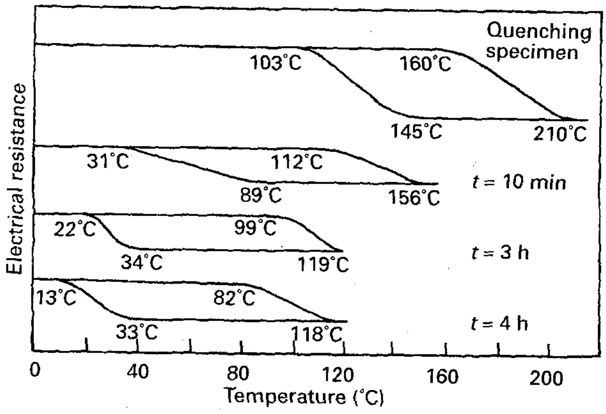

Figure 1 R–T curves for quenched specimens aged at 350 °C for different times (10 min, 3 h and 4 h).

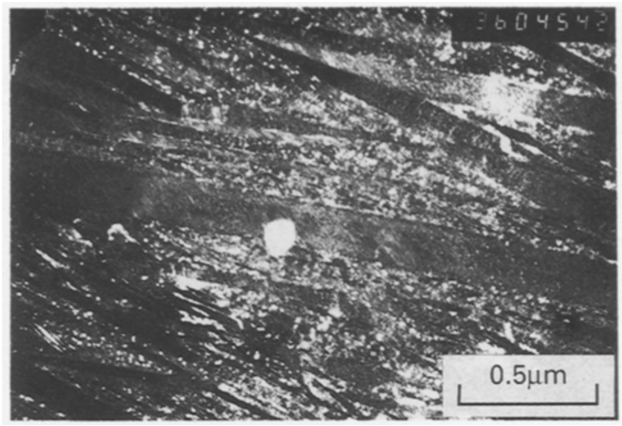

Figure 3 Transmission electron micrograph of a specimen aged at 350 °C for 4 h.

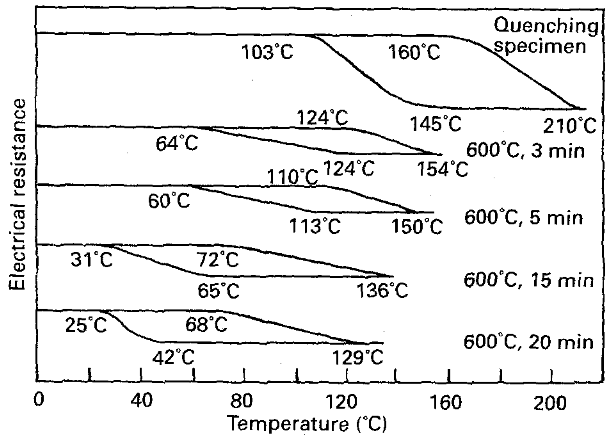

Figure 2 R–T curves for quenched specimens followed by moderate-temperature treatment at 600 °C for different times (3, 5, 15, 20 min).

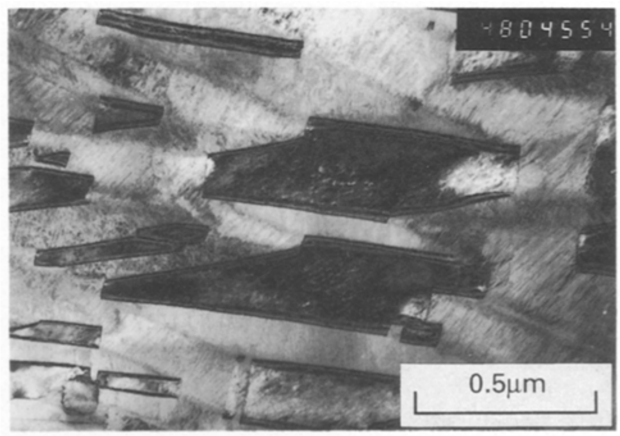

Figure 4 Transmission electron micrograph of a specimen treated at 600 °C for 5 min.

continuously, and the amount of transformation decreases. It should be emphasized that the type of thermo-elastic martensitic transformation changed from type I to type II and then to type I again, according to Wayman's classification [2], and the transformation hysteresis initially decreased and then increased accompanying the change of the type of thermo-elastic transformation.

Transmission electron micrographs of the specimen aged at 350 °C for 4 h are shown in Fig. 3. It can be seen that there are many fine particles dispersed uniformly in the matrix. The selected-area diffraction pattern shows them to have a b c c structure. It can be concluded from the phase diagram that this kind of particle must be NiAl-based precipitation. This is in agreement with the conclusions of Husain and co-workers [3, 4].

Fig. 4 shows transmission electron micrographs of the specimen treated at 600 °C for 5 min. It can be seen that there are some plate-like precipitations in the matrix while the dispersed precipitation, which corresponds to the ageing treatment, cannot be found. The X-ray diffraction pattern of the specimen held at 600 °C for 30 min is shown in Fig. 5. It can be seen that the plate-like precipitations have an f c c structure. According to the phase diagram, it can be concluded

Figure 5 X-ray diffraction pattern of the specimen held at 600 °C for 30 min.

that these plate-like precipitations must be α-phase [5]. This kind of α-phase is rich in copper and nickel and can be easily deformed. The α-phase precipitates preferentially at grain boundaries when the alloy is held at 600 °C, and it can also precipitate within the grain with prolonged holding time, as shown in Figs 6 and 7.

Ageing treatment leads to finely dispersed NiAl-based particles precipitated in the matrix, which will prevent the appearance and disappearance of thermo-elastic martensite, and the self-accommodation relationship is thus destroyed. Hence, the ageing treatment can decrease the transformation temperature of the alloy and enlarge the transformation hysteresis. Because a large amount of NiAl-based particles can

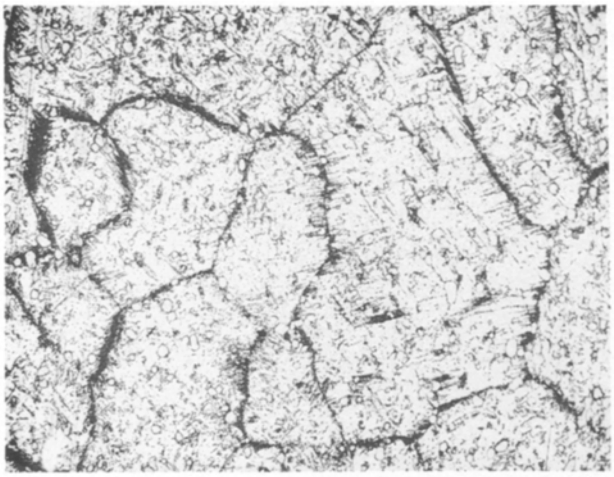

Figure 6 Optical micrograph of a specimen treated at 600 °C for 3 min. × 400

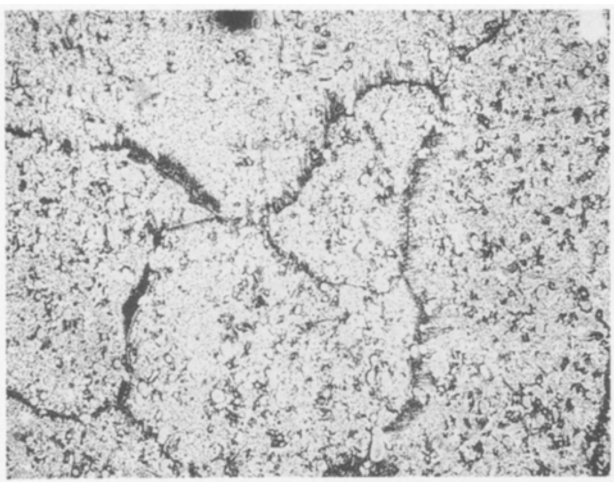

Figure 7 Optical micrograph of a specimen treated at 600 °C for 20 min. × 400

precipitate in the initial stage of ageing at 350 °C, both the amount and size of NiAl-based particles show no great change, hence, the type of electrical resistance temperature curve remains unchanged when the ageing time is prolonged.

The α-phase can precipitate from β-phase when the alloy is treated at 600 °C, the longer the holding time at 600 °C, the greater the amount of the α-phase precipitated, and the less the amount of remaining β-phase which can transfer to martensite. When the alloy is cooled from 600 °C, the unprecipitated β-phase transfers to martensite and no α-phase is formed within the martensite plate. Therefore, the height of the measured electrical resistance versus temperature curve decreases, indicating a decrease in the amount of transformation. The precipitation of α-phase which is rich in copper and nickel atoms can increase the aluminium content remaining in the matrix, so the transformation temperature will be decreased [6]. The type of thermo-elastic martensitic transformation changed from type I to type II and then to type I again, and the transformation hysteresis initially decreased and then increased, accompanying the change of the type of thermo-elastic martensitic transformation. The α-precipitation affects the thermo-elastic behaviour of martensite for the following reasons. α-phase precipitates preferentially at grain boundaries when the holding time at 600 °C is short, and one of the main effects caused by α precipitation is a decrease of M_s as the aluminium content in the matrix is relatively raised. On the other hand, α-phase which possesses an fcc structure is softer than the matrix and can be easily deformed, hence the stress concentration caused by the formation of martensite variants can be released by this kind of grain-boundary α-phase, and transformation hysteresis can be decreased. Thus the type of thermo-elastic martensite transformation changed from type I to type II. When the holding time at 600 °C is prolonged, α-phase will also precipitate inside the grain, and when the volume fraction of α-phase has increased to a high level martensite transformation is retarded. The transformation hysteresis was enlarged for the following reasons: one is the strain constraint effect, the other is the decrease in the amount of β-phase which will transform to martensite.

On the whole, NiAl phase and α-phase have different effects on the transformation hysteresis, and this phenomenon can be explained with respect to the strain constraint and the site of phase precipitation.

4. Conclusions

1. NiAl-based precipitation can form in the matrix uniformly when the CuAlNiMnTi alloy is aged at 350 °C; the transformation temperature will be decreased and transformation hysteresis will be initially increased. Further prolonging the ageing time will decrease the transformation temperature slightly, while both the transformation hysteresis and the type of electrical resistance versus temperature curve remain unchanged.

2. When the alloy is treated at 600 °C, β-phase will decompose, and α-phase can precipitate from the matrix; the longer the holding time at 600 °C, the greater the amount of α-phase precipitated, and the less the amount of remaining β-phase which can transfer to martensite, the less the amount of transformation and hence the lower the height of the electrical resistance versus temperature curve. The α-phase precipitation can decrease the transformation temperature; the type of thermo-elastic martensitic transformation changed from type I to type II and then to type I again, and the transformation hysteresis initially decreased and then increased accompanying the change of the type of thermo-elastic martensitic transformation.

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