Microstructure of CuZnAlMnNi shape memory alloy due to double reversible transformations

LETTER TO THE EDITOR

Microstructure of CuZnAlMnNi shape memory alloy due to double reversible transformations

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Abstract.   A new reversible transformation that is different from the martensite transformation has been found in a calorimetric experiment in CuZnAlMnNi shape memory alloy. The microstructure of the new transformation has been observed by scanning electron microscopy. It is found that the microstructure is a mixture of martensite and a new phase at room temperature. Though the martensite plates transformed from the new phase become thin and sparse, and have irregular morphology due to the incomplete transformation, they still keep the original orientation.

The shape memory effect (SME) is a phenomenon associated closely with martensite transformation. A few studies on the forward and reverse martensite transformation in shape memory alloys (SMAs) have been reported [1–5]. Meanwhile, another reversible transformation named the R-phase transition was observed in TiNiFe SMA [6], whose transformation temperature is above that of the martensite transformation. Although the recoverable strain is limited to 1%, the R-phase transition can be extremely useful for accurate thermal actuators and proportional control devices since the temperature hysteresis is as small as 1.5 K and the temperature–strain curve is quite stable during thermal cycling. However, there were few reports about other reversible transformations at lower temperature except for the martensite transformation in Cu-based SMAs. In this letter, we report a new reversible transformation that is different from the martensite transformation.

The investigated material is a polycrystalline Cu–23.6Zn–4.47Al–0.23Mn–017Ni (wt.%) alloy. The sample was solution treated at 1113 K for 20 minutes, followed by ageing in boiling water for 30 minutes. The DSC-41 differential scanning calorimeter (DSC) was used in the experiment. The experimental parameters are as follows: Al_2O_3 powder for the reference material, 40 ml min^{-1} for the flow rate of nitrogen atmosphere, from 273 to 393 K for the scanning temperature range, liquid nitrogen for the cooling medium, 10 and −10 K min^{-1} for the heating and cooling rate, respectively. In the power compensation DSC measurements, the transformation heat corresponds to the area between the initial and final transformation temperatures on the DSC curve. The endothermic process is assigned with a downward curve, and the exothermic one with an upward curve. The microstructures were observed on a JXA-840 scanning electron microscope (SEM).

Figure 1 shows the DSC curves during heating and cooling between 273 and 393 K. It can be found that two peaks occur on the curves during not only heating but also cooling, though the peak at lower temperature becomes wide and smooth during cooling owing to the

decrease of the cooling rate at low temperature. This denotes the reversibility of the two transformations. The fact that the transformation happening at higher temperature produces an exothermic peak during cooling and an endothermic peak during heating demonstrates that it is the typical martensite transformation. However, the transformation taking place at lower temperature is different from the martensite transformation: it absorbs heat energy during cooling and releases heat energy during heating. Because there is no applied stress imposed on the specimen, the phase transformed from martensite during cooling is not the stress-induced martensite, but a new phase; here we call it the X-phase (whose structure is also unknown. We will investigate it continuously). So the two transformations during cooling are as follows: from parent phase (A) to martensite (M) at higher temperature and from martensite to X-phase at lower temperature. The initial and final temperatures of the two transformations are expressed as M_s, M_f and X_s, X_f respectively; their corresponding values are 327.9, 293.6, 290.1 and 276.8 K respectively. The adverse transformations during heating are from X-phase to martensite at lower temperature and from martensite to parent phase at higher temperature, and the transformation temperatures are X'_s, X'_f and A_s, A_f; their corresponding values are 287.8, 300.3, 304.3 and 355.1 K. The corresponding transformation enthalpies are as follows: $\Delta H_{A \to M} = 225.85$ mJ, $\Delta H_{M \to X} = -11.04$ mJ and $\Delta H_{X \to M} = 28.86$ mJ, $\Delta H_{M \to A} = -314.45$ mJ. It is obvious that the enthalpies of the new transformation are far smaller and its transformation temperatures are lower than that of the martensite transformation. This indicates that the new transformation is non-diffusive as the martensite transformation is. It is interesting to note that the new transformation is almost immediately followed by the martensite transformation.
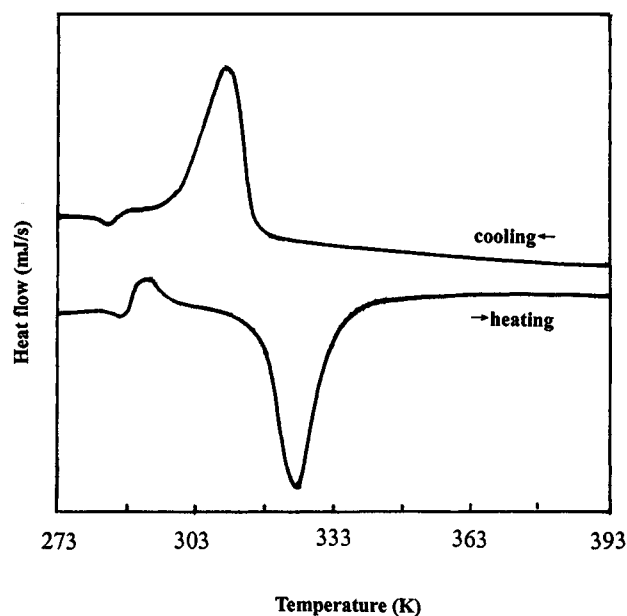

Figure 1. DSC curves during heating and cooling between 273 and 393 K.

In order to observe the variation of microstructure during the new transformation, the specimen after solution treatment was subsequently cooled in liquid nitrogen. The microstructures before and after cooling in liquid nitrogen are shown in figure 2. It can be found from figure 2(a) that the microstructure after solution treatment is the typical spear-like
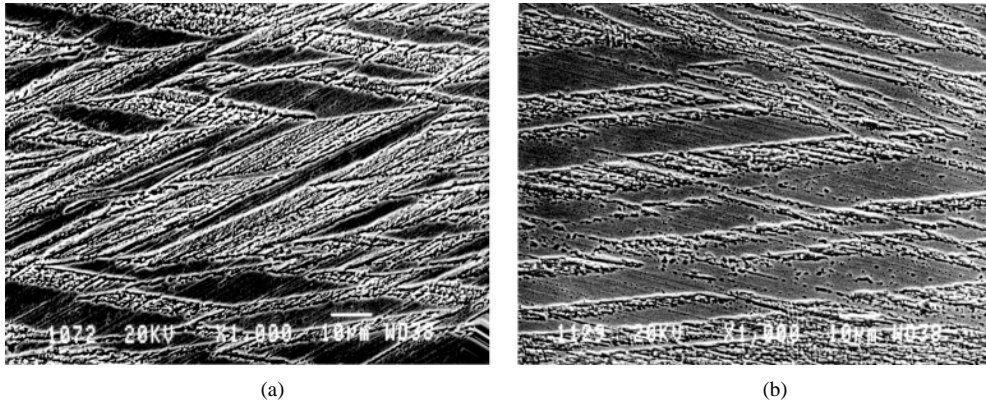
Figure 2. SEM microstructures of the CuZnAlMnNi alloy at 291 K. (a) After solution treatment. (b) After cooling in liquid nitrogen.

martensite. However the microstructure after cooling in liquid nitrogen, as shown in figure 2(b), has changed markedly. Although the spear-like martensite can be observed vaguely, the amount of martensite obviously decreases, the martensite plates become thin and sparse and have irregular morphology with respect to that in figure 2(a). This is because at room temperature (291 K or so), the specimen is just in the middle of the transformation stage from X-phase to martensite: part of the X-phase has transformed into martensite. Thus the microstructure at this moment is a mixture of martensite and X-phase. It is evident that the X-phase does not have the spear-like morphology, while the martensite transformed from the X-phase still has the spear-like morphology. The thin and sparse martensite plates, as well as the irregular plate morphology, are caused by the incomplete transformation from X-phase to martensite. This further denotes the reversibility of the new transformation. It can also be found that the martensite plates transformed from the X-phase still keep the original orientation and this is another verification that the new transformation is non-diffusive.

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