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Short note

Temperature memory effect in CuAlNi single crystalline and CuZnAl polycrystalline shape memory alloys

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Abstract

Temperature memory effect (TME) induced by incomplete cycling in CuAlNi single crystalline and CuZnAl polycrystalline shape memory alloys were investigated by differential scanning calorimeter. Results showed that the TME is a common phenomenon in shape memory alloys, caused by a partial martensite to parent phase transformation.

Keywords: Shape memory alloy; Martensitic phase transformation; Differential scanning calorimetry (DSC); Temperature memory effect

1. Introduction

Shape memory alloys (SMAs) have attracted considerable interest as potential candidates for novel engineering and mechanical applications owe to their excellent functional properties, shape memory effect and superelasticity behavior. SMAs also exhibit a unique property of memorizing the point of interruption of martensite to parent phase transformation. An incomplete thermal cycle upon heating of SMAs (arrested at a temperature between austenite transformation start and finish temperatures, A_s and A_f) induced a kinetic stop in the next complete thermal cycle. The kinetic stop temperature was closely related to the previous arrested temperature. So this phenomenon is named temperature memory effect (TME) [1]. Previously this phenomenon was also named thermal arrest memory effect [2] or step-wise martensite to austenite reversible transformation [3,4]. The TME was firstly reported in thermally induced phase transformation in TiNi alloys [5]. The TME can be wiped out by heating the SMAs to a temperature higher than A_f. The TME phenomenon has also been found in stress-induced transformation [4]. However, the TME in the stress-induced transformation cannot be erased by conducting complete mechanical–thermal cycles, but can be erased through an appropriate thermal treatment [4]. We have systematically studied the TME of TiNi-based shape memory alloy [6]. There is little report on the TME in Cu-based shape memory alloy, especially in single crystalline SMAs. Though this phenomenon has been subject of intensive investigation, a satisfactory explanation is still at large. The purpose of the present work is thus to determine whether there is a TME in Cu-based shape memory alloy or not and to discuss the origin of the TME.

2. Experiments

The investigations have been carried out on Cu–21.5 wt.% Zn–5.85 wt.% Al SMA with a thickness of 0.80 mm and Cu–14 wt.% Al–4.2 wt.% Ni with a thickness of 1.0 mm. The CuZnAl were annealed at 760 °C for 7 min and quenched in the water at 100 °C. The CuAlNi were annealed at 810 °C for 20 min and quenched in the oil at 120 °C. The grain size of CuZnAl is about 500 μm after the heat treatment. The temperature memory effect was also measured using DSC (DSC131, Setaram Company, France) with a scanning rate of 10 °C/min under nitrogen atmosphere. Temperature and enthalpy calibration was performed using In, Sn and Zn as the calibrant. The arrested temperature is denoted as T_s hereafter. The transformation temperatures of these two samples are shown in Table 1. The DSC was programmed for the following thermal cycle: (i)

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Table 1
Transformation temperatures of the CuZnAl and CuAlNi samples

Samples	A_f (°C)	A_s (°C)	M_s (°C)	M_f (°C)
CuAlNi	66.5	48	53	41
CuZnAl	81	70	69	57

cool to below M_f; (ii) heat to a temperature T_s, which is located between A_s and A_f; (iii) cool to below M_f; (iv) heat to above A_f.

3. Results and discussion

The complete and incomplete transformation behaviors of CuZnAl polycrystals are shown in Fig. 1(a). In order to make the TME more evident, the derivatives of the heat flows upon heating are shown in Fig. 1(b). Those of CuZnAl with single incomplete cycle upon heating at T_s = 73.9 and 76.2 °C, respectively, are shown in Fig. 1(i) and (ii), and the kinetic stops are clearly observed on the heat flow curves upon heating. Fig. 1(iii) shows the DSC results of CuZnAl after performing two successive incomplete cycles upon heating at temperatures of T_s = 73.8 and 76.3 °C with sequential ordering, and only one kinetic stop can be clearly seen corresponding to the maximum temperature of T_s = 76.3 °C. Two kinetic stops can be clearly observed after performing two successive incomplete cycles upon heating at two arrested temperatures of T_s = 76.3 and 73.8 °C with sequential ordering, as shown in Fig. 1(iv). The phenomenon shows that only the highest temperature of the two successive temperatures is memorized, which implies that further heating to a temperature exceeding the previous stop temperature can wipe out the temperature memory effect caused by the previous stop temperature. The above results consist with those from previous reports [7]. If a number N of ICHs with different arrested temperatures is performed in a decreasing order, N interruptions can be found.

The complete and incomplete transformation behaviors of CuAlNi single crystals are shown in Fig. 2(a). And the corresponding derivatives of the heat flows upon heating are shown in Fig. 2(b). The single kinetic stops are also clearly observed on the heat flow curves upon heating after performing single incomplete cycle upon heating at T_s = 57.0 and 58.9 °C, respectively. Three kinetic stops can be clearly observed after performing three successive incomplete cycles upon heating at three arrested temperatures of T_s = 59.4, 58.0 and 56.5 °C with sequential ordering.

The above results show that the TME appear in both single crystals and poly crystals after performing the incomplete reverse M → P transformation. However, TME in single crystals is less evident than in polycrystals, as already shown in previous literature results on CuZnAl single crystals [8], this result indicate that the grain boundaries also have contribution to the TME.

When the transformation from the martensite to austenite transformation is stopped at a certain temperature T_s, only part of the martensite transforms into the parent phase, while the rest of the martensite remains, called M1. When the temperature decreases below M_f, the parent phase transforms back into martensite that is defined as M2. The M2 and M1 transform into the parent phase sequentially, with a kinetic stop between them for the next heating. It has been suggested that the TME is associated with elastic strain energy, which serves as the driving force

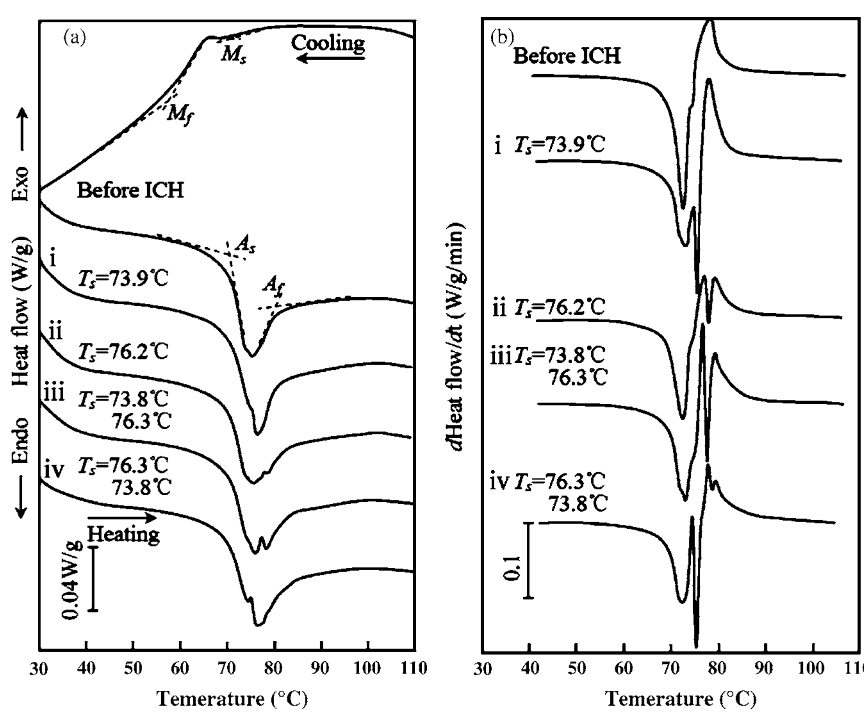

Fig. 1. Temperature memory effect in CuZnAl polycrystals with single incomplete cycle on heating at T_s = 73.9 and 76.2 °C and two successive arrested temperatures of T_s = 76.3 and 73.8 °C with sequential ordering or T_s = 73.8 and 76.3 °C with sequential ordering. (a) Heat flow vs. temperature and (b) derivation of heat flow vs. temperature.

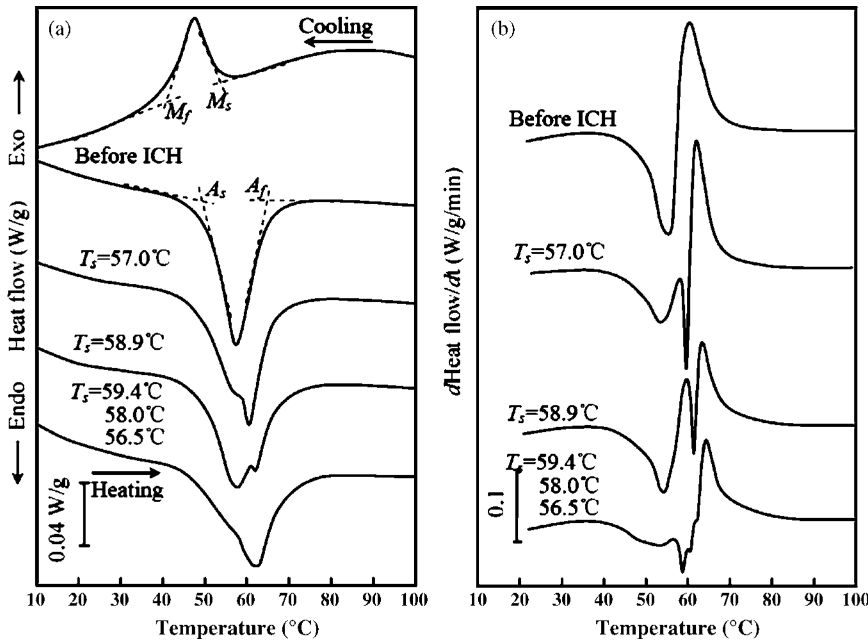

Fig. 2. Temperature memory effect in CuAlNi single crystals with single incomplete cycle on heating at $T_s = 57.0$ and $58.9\,^\circ$C and three successive arrested temperatures of $T_s = 59.4$, 58.0 and $56.5\,^\circ$C with sequential ordering. (a) Heat flow vs. temperature and (b) derivation of heat flow vs. temperature.

during the reverse transformation [9]. Airoldi [4] explained the TME by the lack of elastic strain energy in M2. Therefore, a higher temperature is necessary to finish the transformation of M2 and to start the transformation of M1. The results obtained by Zheng et al. [1] show that the formation of M2 is due to the nucleation and growth of martensite nuclei in the parent phase, but not the growth of the existing M1 martensite. Otherwise, M2 should have the same oriented structures as M1, if the growth of M2 is based on M1. So M1 and M2 transform into parent phase at different temperatures for the next heating process.

The free energy of the nucleation of a plate of martensite is given as [10]: $\Delta G^{\mathrm{Nucl}} = \Delta G^{\mathrm{Chem}} + \Delta G^{\mathrm{Non\text{-}chem}} + \Delta G^{\mathrm{Interface}}$. In the case of ordered shape memory alloys, a reduction in ΔG^{Nucl} can be achieved by the minimization of $\Delta G^{\mathrm{Non\text{-}chem}}$ by the formation of self-accommodating variants. And elastic strain energy will be stored in the thermoelastic martensite variants. During the transformation from B2 phase to martensite phase, the interphase boundaries between the martensites and the parent phase are coherent phase boundaries, called the habit planes, and the coherent energy resulting from the lattice distortions at the coherent interfaces has a prominent effect on the transformation characteristics [11]. When the martensite to austenite transformation is stopped at a certain temperature T_s, only part of the martensite transforms into the parent phase. There exists coherent stress between the two phases. When the temperature decreases below M_f, the parent phase transforms back into martensite. Using *in situ* TEM, Bataillard et al. [12] observed that B19’ martensite nucleate from stress regions and then grow into the matrix (stress free region). New orientation martensite M2 will form which are favored by these coherent stresses. Fig. 3 schematically shows the TME in shape memory alloys. Upon heating part of the martensite transforms to parent phase with M1 martensite phase remains. M2 martensite phase forms upon cooling, domain walls appear between the M1 and M2 martensite phase. The newly formed M2 martensite at the M1–M2 interface will accommodate itself to decrease the elastic strain energy level. This leads to the release of the stored elastic strain energy in M1 at the M1–M2 interface. As the first formed martensite plate is the last to revert to the parent phase and the last formed plate is the first to [13], and much more work to overcome the domain walls motion. So the release of the elastic strain energy and more work to overcome the motion of domain walls lead to the transformation of M1 shift to higher temperature and a kinetic stop appears upon heating. There exist much grain boundaries in polycrystals, the work need to overcome the motion of domain walls are larger than in the single

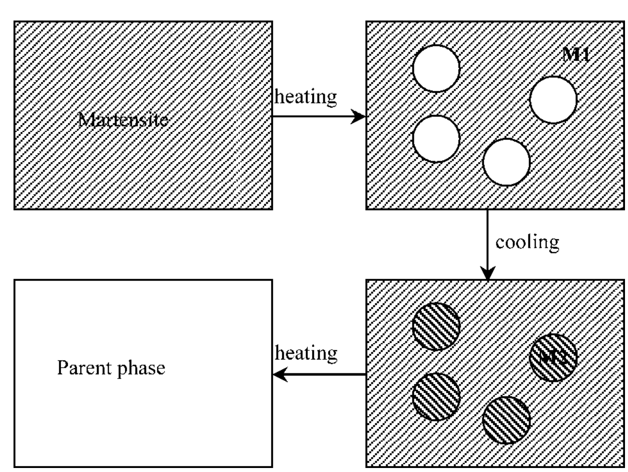

Fig. 3. Schematic diagram of TME in shape memory alloys. Upon heating part of the martensite transforms to parent phase with M1 martensite phase remains. M2 martensite phase forms upon cooling, M2 and M1 transformed to parent phase sequentially upon heating.

crystals. So TME in polycrystals is more evident than in single crystals.

4. Conclusions

In this work, the TME induced by incomplete cycling in CuAlNi single crystal and CuZnAl polycrystal was investigated by performing either a single incomplete cycle, or a sequence of incomplete cycles with different arrested temperatures. The results showed that TME is common phenomenon in shape memory alloys, which is induced by a partial reverse $M \rightarrow P$ transformation. TME in polycrystals is more evident than in single crystals. The decrease of elastic energy after ICH procedure and the motion of domain walls have significant contributions to the TME.

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