



# Athermal nature of the martensitic transformation in Heusler alloy Ni–Mn–Sn

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## ABSTRACT

Martensitic transformations are generally classified into two groups, namely athermal and isothermal, according to their kinetics. In case of athermal transformations, the amount of the product phase only depends on temperature, and not on time. However, much debate rises about this issue due to unexpected experimental observations of isothermal effects in typically athermal transformations. Considering that the wide applications of Heusler Ni–Mn based materials are based on martensitic transformations, it is of importance to clarify the nature of their martensitic transformation. In this paper, we made an effort to study isothermal effects in a Ni–Mn–Sn alloy using differential scanning calorimetry (DSC). It is proposed that the martensitic transformation of Ni–Mn based materials is athermal in nature although a time-depending effect is observed through DSC interrupted measurements.

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## 1. Introduction

Since the shape memory effect and superelastic behavior based on martensitic transformation (MT) in Ti–Ni alloys were published in 1963 [1], this type of solid-state transformation has attracted considerable attention. Martensitic transformations are generally classified into two groups with respect to their kinetics, athermal and isothermal transformations [2,3]. In case of athermal transformations, the amount of the product phase only depends on temperature, but not time. This is due to its intrinsic nature, since the transformation does not involve diffusion, and the composition of the product is the same as that of the parent phase. A cooperative movement of many thousands of atoms occurs with a velocity approaching that of sound waves in the crystal. What is accepted about the athermal transformation leaves little space for time dependence. Recently, some unexpected findings on time-dependent behaviors in typically assumed athermal transformations occurring just above the  $M_s$  temperature were reported. Meanwhile, some contradicting experimental results and discussions have led to even more debates about this issue. Kozuma et al.

found that the electric resistance of a quenched Au–49.5 at.%Cd alloy increased considerably when holding at a temperature of 1 K above the  $M_s$  temperature, which was confirmed due to the formation of substantial isothermal martensite nuclei, and they ascribed to the annihilation of excess vacancies during isothermal holding [4]. As for Ni–Ti shape memory alloys with B2 → R → B19' two-stage martensitic transformations, Kustov et al. [5] observed that both direct B2 → R and reverse R → B2 transformations were perfectly athermal, whereas isothermal formations of B19' martensite and R phase were detected in R ↔ B19' transformations. Both fcc ↔ fct transformations in In–Ti [6] and B2 ↔ β' transformations in Ni–Al [7] exhibited time-dependent kinetic characters. Very recently, we observed a time-depending effect in B2 → R transformation in a Ti<sub>50</sub>Ni<sub>47</sub>Fe<sub>3</sub> alloy using differential thermal analysis technique and ascribed these observations to changes in transformation temperatures [8].

Isothermal features were also found in ferromagnetic shape memory materials. With the application of high magnetic fields, Kakeshita et al. observed that the electric resistivity decreased dramatically after isothermal holding for 1020 s at the temperature of ( $M_s + 6$  K) in Fe–31.7%Ni, and the incubation time for the formation of martensite in Fe–24.0Ni–4.3Cr decreased remarkably as the magnetization of martensite is much higher than that of the parent phase [9]. A polycrystalline Ni<sub>50</sub>Mn<sub>29</sub>Ga<sub>21</sub> was studied by isothermal holding for 20 h in the phase transition region, both

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forward and reverse martensitic transformations demonstrated isothermal behaviors [10]. Furthermore, the forward transition from ferromagnetic austenite to nonmagnetic martensite demonstrated isothermal features, the reverse one is athermal in the metamagnetic shape memory alloy  $\text{Ni}_{50}\text{Mn}_{34.3}\text{In}_{15.7}$ . The asymmetry was attributed to the change in the magnetic ordering accompanying the first-order lattice modification, thus the change opposed the forward transition and promoted the reverse one [11]. Driven by the combination of magnetic field and temperature, the incubation time is strongly depended on the holding temperature, with shorter incubation time when holding near the  $M_s$  temperature [12].

Kakeshita et al. [13] proposed a phenomenological model based on thermal fluctuations to explain both athermal and isothermal transitions in a unified way, *i.e.*, both transitions were isothermal in nature, and the incubation time of athermal transition was too short to observe. This was well demonstrated in Fe–Ni–Cr alloys, where isothermal and athermal transitions could convert to each other under the influence of external magnetic field and hydrostatic pressure, exhibiting no fundamental difference between the two processes [14]. This model was also applicable to the isothermal accumulation of martensite/austenite in ferromagnetic Ni–Co–Mn–In alloys [15]. However, Otsuka et al. [16] proposed that the isothermal martensitic transformation may be closely linked to the interaction between the immigration of atoms/vacancies and the displacive transformation. It was verified by a seminal experiment performed in Ni–50 at.%Ti alloys with extremely low diffusion around the transformation temperature, where no isothermal accumulation of martensite was observed at temperatures of  $M_s + 1.5$  K and  $M_s + 1.6$  K, respectively, which were slightly above the  $M_s$  temperature with annealing time lengthened to 21 days. Planes et al. [17] developed an alternative model that the  $M_s$  temperature was not consistent, but a stochastic variable distributed in a temperature interval, and the transformational character was intimately connected to external conditions. For example, an isothermal martensitic transformation occurred in Cu–Al–Ni shape memory alloys at cooling rates above 30 K/min, while athermal nature was observed below 30 K/min. Planes et al. [17] pointed out that thermal fluctuations are effective in a small temperature interval, depending on certain time scales directly related to the experimental conditions. Isothermal and athermal natures are not intrinsic, which is in accordance with the model of Kakeshita et al. [13].

Today, a large number of applications are developed from these types of materials based on their solid-state martensitic transformations. Therefore, it is of importance to understand the phase transformation in a certain alloy for its practical applications. As stated in Ref. [17], most of the previous research was conducted by holding the sample slightly above the  $M_s$  temperature and monitoring the change in electric resistivity, etc., and the following problems were inevitable to avoid: (1) the  $M_s$  temperature may depend on the cooling rate; (2) the  $M_s$  temperature may differ significantly from one cycle to another even if they are performed at the same rate. Therefore, in this study we chose a Heusler Ni–Mn–Sn ribbon material with perfect thermal reproducibility, and high-resolution thermal analysis technique was employed to circumvent the above mentioned problems. The scientific objective is to reveal the nature of martensitic transformation occurring in Ni–Mn–Sn alloys, which has the applications in magnetic refrigeration. Among the family of Heusler Ni–Mn based materials [18–22], Ni–Mn–Sn is more attractive due to its potential for large-scale engineering applications [21,22].

## 2. Materials and experimental procedures

The material used in the present study is a  $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$  (at.%) ribbon which was produced through melt spinning. The

preparation procedure has been described in detail in Ref. [21]. The  $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$  was annealed at 1273 K for 4 h for homogenization followed by water quenching.

Differential scanning calorimetry (DSC) measurements were performed using a high-resolution Netzsch 204 F1 DSC instrument, which was calibrated carefully before the actual experiments. The sample (63.2 mg) was firstly subjected to 10 heating and cooling cycles at a temperature-rate of 10 K/min, and the results show that thermal cycling almost exhibits no effect on the transformation behavior, as shown in Fig. 1. In this regard, a single sample can be used in the following DSC measurements without the concern of transformational changes caused by cycling. Similar results have been reported in  $\text{Ni}_{49}\text{Mn}_{39}\text{Sn}_{12}$  with 30 cycles [22]. Large exothermic and endothermic peaks are associated with direct martensitic and reverse transformations [21]. The characteristic transition temperatures consisting of the forward martensite start and finish temperatures ( $M_s$ ,  $M_f$ ) upon cooling are determined to be 243.5 K and 221 K, respectively. While those of the reverse transformation ( $A_s$ ,  $A_f$ ) upon heating are 252.5 K and 279 K, respectively.

In the present study, the transformation behavior was analyzed through DSC interrupted experiments. These experiments were conducted such that the sample was initially heated to 323 K, held for 5 min, and then cooled down to 247 K and 245 K, respectively. After holding the sample for different times varying from 0 to 90 min at 247 K/245 K, the material was again heated to 323 K to complete the DSC tests. The heating/cooling rate during the thermal process is either constantly 10 K/min or as indicated. Fig. 2a shows the actual temperature–time curves of the DSC interrupted experiments performed at 247 K and an enlargement is given in Fig. 2b, where one can notice that once the sample begins holding during the cooling process, the temperature quickly reaches to the preset temperature and the largest forward fluctuation is 0.45 K.

## 3. Results and discussion

When the DSC measurements are interrupted at 245 K and 247 K, no martensite is expected to form during this process since the temperature is higher than the  $M_s$  temperature. However, the DSC results show that a small volume fraction of martensite has formed during the holding process, as evidenced from the clear endothermic peaks appearing upon heating (Fig. 3). For the measurements interrupted at 247 K, a small endothermic peak can be observed after holding for 30 min, and with extending time to 90 min, the peak appears further enhanced (Fig. 3a). In case of 245 K, the formation of martensite is more quickly since the endothermic peak already appears after 2 min holding, and more martensite appears within the same holding time as indicated

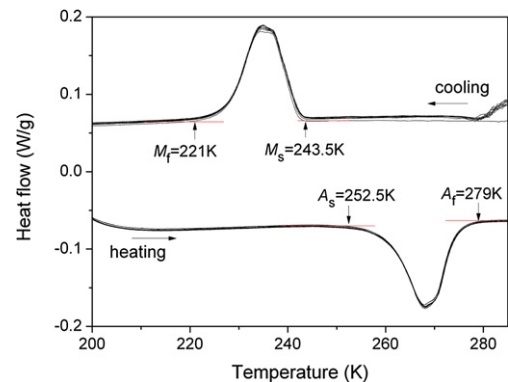


Fig. 1. Ten cyclic DSC curves of  $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$  demonstrating perfect thermal reproducibility.

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