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# New observations on the thermal arrest memory effect in Ni–Ti alloys

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#### Abstract

Ni–Ti shape memory alloys demonstrate a unique phenomenon known as thermal arrest memory effect or TAME. In the present work, a new observation regarding the nature of this phenomenon in Ni–Ti alloys has been made. It is observed that the thermal arrest of the reverse transformation causes the endotherm of the pre-existing martensite microstructure to drift up to 9 K above the reverse transformation temperature of the alloy. The analysis suggests that this could be due to the growth of the pre-existing primary martensite plates.

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Keywords: Ni-Ti; Martensite; Shape memory effect; TAME

### 1. Introduction

Shape memory alloys exhibit a unique propensity of memorizing the point of interruption of the martensite to parent phase (M–P) reverse transformation [1,2]. Though this phenomenon, variously known as the thermal arrest memory effect (TAME) [1] and stimulated martensite to austenite reverse transformation (SMART) [2–5], has been the subject of intense investigations [1–7], a satisfactory explanation is still at large. The main aim of the present work is to determine the effect of thermal arrest on the transformation of the pre-existing microstructure.

## 2. Experimental

Equiatomic Ni–Ti alloy was prepared from high purity nickel and titanium by non-consumable vacuum arc melting. The alloy buttons were hot rolled at 1123 K

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into sheets of 1 mm thickness. The material was annealed and subsequently pickled to remove the surface oxide. Differential scanning calorimetry (DSC) and transmission electron microscopy were used to examine the samples obtained from these sheets.

To generate an event of the TAME, the DSC was programmed for the following thermal cycle [1]: (i) cool to below  $M_{\rm f}$ ; (ii) heat to a temperature between  $A_{\rm s}$  and  $A_{\rm f}$ ; (iii) cool to below  $M_{\rm f}$ ; (iv) heat to above  $A_{\rm f}$ .  $M_{\rm s}$ ,  $M_{\rm f}$ ,  $A_{\rm s}$  and  $A_{\rm f}$  here have the usual meaning, i.e. they are the characteristic temperatures of the martensite transformation. The experiment is preceded by a complete cooling-heating cycle to 'wipe' away any memory of previous arrests. On cooling to  $M_{\rm f}$ , (i), the parent phase transforms completely to martensite (P-M), while during heating, (ii), the reverse transformation to the parent phase (M–P) commences at  $A_s$ . At the point of thermal arrest some fraction of the original martensite microstructure would have transformed to the parent phase which, during the subsequent cooling step, (iv), will transform back to martensite. The difference in the transformation behaviour of the original and the later martensite microstructures causes the TAME in step (v).

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#### 3. Observations and discussion

As shown schematically in Fig. 1(e)–(f), when the M–P transformation is arrested at a temperature between  $A_s$  and  $A_f$  and cooled to below the  $M_f$ , the endothermic M–P peak in the second heating cycle splits into a doublet centered at the point of arrest in the previous cycle. In the case of multiple thermal arrests, the M–P endothermic peak splits into as many peaks marking each point of arrest [2]. Interestingly, TAME has a mechanical analogue [4], wherein the point of arrest of the pseudoelastic M–P transformation during unloading is "memorized" by a noticeable load drop.

There are two different views on the origin of this effect. Airoldi and co-workers [2-5] suggest that this phenomenon is related to the hysteresis associated with the martensite transformation. Thus, they show that the TAME is more pronounced in alloys in which the transformation is associated with a larger hysteresis. The other view held by Madangopal et al. [1], Fig. 1(a)–(d), is that this phenomenon is a consequence of the unaccommodated transformation shape strain (UTSS) of the untransformed prior martensite microstructure (population I or pI) influencing the subsequent P–M transformation (population II or pII).

The free energy of the nucleation of a plate of martensite is given as [8]:  $\Delta G^{\text{Nucleation}} = \Delta G^{\text{Chemical}} + \Delta G^{\text{Non-Chemical}} + \Delta G^{\text{Interface}}$ . In the case of ordered shape memory alloys, a reduction in  $\Delta G^{\text{Nucleation}}$  can be achieved by the minimization of  $\Delta G^{\text{Non-Chemical}}$  by the formation of self-accommodating plate-groups [8]. The transformation shape strain (TSS) thus "locked-in" or accommodated biases the P-M to occur at lower temperatures [9]. On the other hand, the unaccommodated part of the TSS will act as a barrier to nucleation and, therefore, the plate group associated with highest locked-in TSS, i.e. the most self-accommodating one, will be preferred to form [10]. During the course of transformation, the UTSS that is built up by one generation of plate-groups will need to be accommodated or "mopped up" by subsequent ones. The picture that emerges is that the martensite microstructure is built up of a hierarchy of generations, each different from the other in terms of the locked-in TSS. The last formed plate group and the first formed plate group in this microstructure will be the most biased and the least biased, respectively, in terms of the locked-in TSS. This explains why, the first formed martensite plate is the last to revert and the last formed plate is the first to [11]. Such considerations also led Tong and Wayman [11] to suggest that  $T_0$ , the temperature at which the chemical driving force of the P-M and the M-P transformations are equal, lies between  $A_{\rm f}$ , and  $M_{\rm s}$ , i.e.  $T_0 =$  $1/2(A_{\rm f}+M_{\rm s})$ . The situation at  $M_{\rm s}$  in the cooling cycle following the thermal arrest, Fig. 1(f), where the newly formed parent phase transforms to pII, is different from that when the microstructure is composed of only the parent phase, Fig. 1(a)-(b). Here, the first plate-groups that form are influenced by the UTSS of pI. This effect appears to diminish with further transformation, as  $A_s$ 

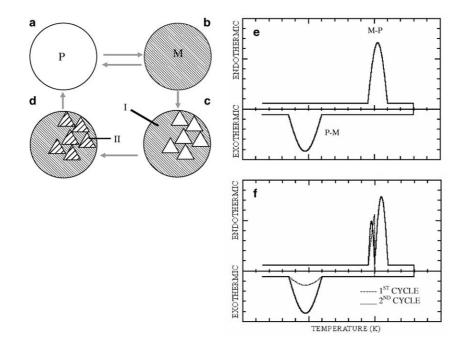


Fig. 1. Schematic explaining the TAME: (a)–(b) The transformation of a single crystal of the parent phase (P) to polyvariant martensite microstructure (M) and (e) the corresponding exotherm and endotherm; (a)–(b)–(c)–(d) the parent phase created in the thermal arrest of M–P transformation (dotted line in (f)) transforms, on cooling, to martensite population II; (f) the endotherm of the 2nd heating cycle shows a doublet centered at the temperature of arrest in the first M–P transformation cycle.

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