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Thermally Activated Martensite: Its Relationship to Non-Thermally Activated (Athermal) Martensite

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THERMALLY ACTIVATED MARTENSITE: ITS RELATIONSHIP TO NON-THERMALLY ACTIVATED (ATHERMAL) MARTENSITE

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Abstract

The classification of martensitic displacive transformations into *athermal*, *isothermal* or *anisothermal* is discussed. *Athermal* does not mean “no temperature dependence” as is often thought, but is best considered to be short for the notion of *no thermal activation*. Processes with no thermal activation do not depend on time, as there is no need to wait for sufficient statistical fluctuations in some specific order parameter to overcome an activation barrier to initiate the process. Clearly, this kind of process contrasts with those that are thermally activated. In the literature, thermally activated martensites are usually termed *isothermal martensites*, suggesting a constant temperature. Actually such martensites also typically occur with continuous cooling. The important distinctive feature of these martensites is that they are thermally activated and hence are distinguishable in principle from *athermal* martensites. A third type of process, *anisothermal*, has been introduced to account for those transformations which are thought to be thermally activated but which occur on continuous cooling. They may occur so rapidly that they do not appear to have an incubation time, and hence could be mistakenly called an athermal transformation. These designations will be reviewed and discussed in terms of activation energies and kinetic processes of the various martensitic transformations.

Terminology

The kinetics of thermodynamic first order martensitic phase transformations are usually designated as being either athermal or isothermal. *Athermal* is an adjective for the kind of phase transformation which is not (hence the *a*) thermally activated, i.e. in athermal transformations there is no thermal activation necessary for the transformation to proceed. *Athermal* transformations therefore do not depend on *time* but depend on and proceed with change in temperature. The word *isothermal* (*same heat*) is used as an adjective for a transformation that occurs at a constant (*same*) temperature. When used in martensitic transformations, isothermal refers to those transformations which proceed with time and are therefore contrasted with *athermal transformations*, since they (isothermal martensitic transformations) are thermally activated [1, 2]. From this we see that the term *thermal* describes different concepts in the words iso*thermal* and a*thermal*. In isothermal, *thermal* is being used to signify “temperature”, while in athermal, *thermal* is short for “thermally activated.”

Thus, the literature contrasts *isothermal* with *athermal*, but not all non-athermal transformations are necessarily isothermal! There may be thermally activated processes which occur on continuous cooling. These have been called *anisothermal* [3].

Anisothermal transformations are thermally activated processes that occur during continuous cooling. Two cases may be distinguished, namely those that occur during:

1. Moderate Cooling Rates
2. High Cooling Rates

The high cooling rate transformations could be confused with athermal transformations. They can be distinguished from athermal transformations if the alloy is allowed to remain at the temperature for a time; if further transformation occurs the transformation was a thermally activated process and therefore anisothermal. Thus, we include *anisothermal* to keep the distinction between processes that occur without thermal activation (athermal) and with thermal activation.

Since athermal refers to transformations which occur without the need for thermal activation, and since they are contrasted with isothermal martensitic transformations, we suggest that the term “isothermal martensite” be replaced with the term: Thermally Activated Martensite (TAM). Thermally Activated Martensite is martensite which has been formed by a process that requires thermal activation (whether it was formed isothermally or during continuous cooling). This would better denote the essential character of such transformations, namely that they involve thermally activated processes.

Initiation and Growth

The two important processes in a first order phase transformation are the initiation and growth of the new phase. In Table I, we divide phase transformations into four categories, depending on which, if any, of these two processes is thermally activated. Diffusion controlled precipitation reactions have thermal activation for both the initiation stage and the growth stage of the transformation. They are therefore time dependent and their TTT (time-temperature-transformation) curves display the well know C-curve behavior. Thermally activated martensitic transformations have thermal activation only at the initiation stage, as the growth stage normally occurs rapidly and without the need for thermal activation. Thermally activated martensitic transformations also display C-curve behavior in their TTT diagrams. In contrast, athermal martensitic transformations have no activated processes. Athermal martensitic transformations do not need time to proceed, only a sufficient thermodynamic driving force obtained by lowering the temperature. A fourth possibility is included in the table, namely one in which the initiation stage does not need thermal activation but the growth stage does. This would be the case for diffusion controlled precipitation reactions that grow from pre-existing nuclei. Of course there could be thermally activated martensitic transformations which have thermal activation in their growth as well as in their initiation process. These too would have C-curve behavior and would be difficult to distinguish from the normally observed “isothermal martensite”.

Table I. Thermal Activation of Phase Transformation Processes

	Thermal Activation for Initiation	**Thermal Activation for Growth**
Classical Precipitation	Yes	Yes
Thermally Activated Martensite	Yes	No
Athermal Martensite	No	No
Diffusion controlled growth from preexisting nuclei	No	Yes

TTT Curve Representation

The well known C-curve shape for isothermal thermally activated precipitation reactions is plotted on a TTT diagram shown in Figure 1a. The time to form the new phase initially decreases as the temperature is lowered from the equilibrium transformation temperature due to the decrease in the barrier to nucleation, as shown in Figure 1b. This decrease in the nucleation barrier occurs because the thermodynamic driving force increases as the material is cooled to lower temperatures. However the time to form the new phase begins to increase at lower temperatures, due to the lack of thermal energy necessary for diffusion to take place. In terms of the thermally activated processes, nucleation controls the upper region of the C-curve while diffusion controls the lower region of the curve.

The C-curve behavior on TTT diagrams of the thermally activated martensitic transformations (See Figure 2a) cannot be explained in the same way as precipitation transformations, since there is little or no activation barrier to growth in thermally activated martensitic transformations. Of course all thermally activated processes must cease at zero Kelvin, but the TTT curves for thermally activated martensitic transformations bend back well above zero Kelvin. Thus, it appears that the barrier to nucleation must also have the shape of a C-curve if it controls the transformation kinetics. Since this barrier has within it the elastic energy of the transformation, such an increase in barrier could come about because of an increase in the elastic stiffness of the matrix at very low temperatures. This has been discussed by Lobodyuk and Estrin [4].

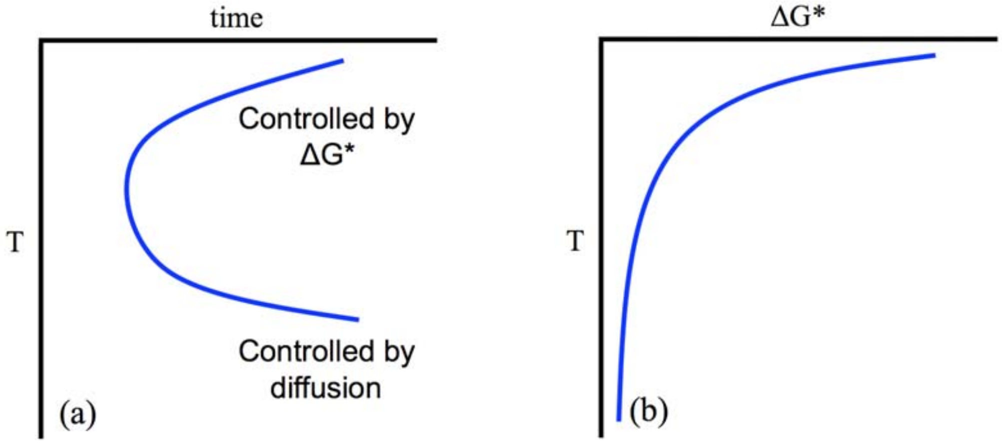

Figure 1. Schematic of (a) a typical TTT curve for a diffusion controlled precipitation transformation and (b) a plot of ΔG*, the barrier to nucleation, vs. T for precipitation.

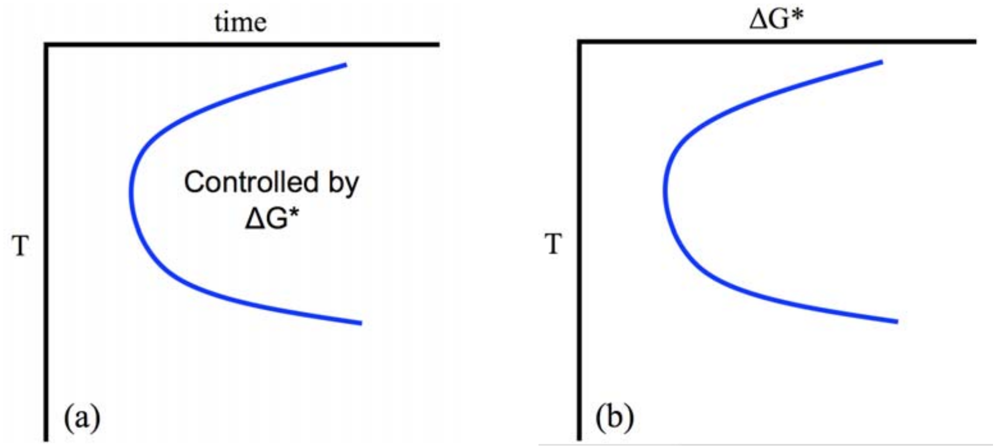

Figure 2. Schematic of (a) a typical TTT curve for a thermally activated martensitic transformation and (b) a plot of the smallest ΔG* for the given undercooling vs. T for a thermally activated martensitic transformation.

Sequences of Martensitic Transformations

Lin, Olson and Cohen have postulated based on thermodynamic and kinetic calculations that in the alloy FeNi there exists a composition and temperature in which athermal martensite first forms followed by anisothermal martensite which in turn is followed by isothermal martensite [5]. This led us to consider the possible sequences of different types of martensitic transformations. The Relative Position of M_s and the Nose of the TAM Curve, and the rate of cooling allow for several possible sequences of transformations (See Figure 3).

In Figure 3 we plot various cooling curves on the TTT diagram. We realize that this depiction is not completely accurate in that continuous cooling transformation curves would be somewhat different from the isothermally derived TTT curves, but for the sake of simplicity we will use this approximation.

Consider Figure 3a. In this figure the M_s temperature for athermal martensite is above the knee of the TTT curve, but below the highest temperature that thermally activated martensite can form, M_{si} [6]. Cooling curve 1 represents the sequence of an athermal marstensitic transformation followed by an isothermal martensitic transformation. In contrast to this, curves 2 and 3 represent transformations which proceed from athermal to anisothermal to isothermal. This is because the isothermal hold temperature was not reached before the material passed through the TTT curve allowing for some thermally activated process to occur during the continuous cooling before the isothermal martensite begins to form.

Figure 3b displays a TTT curve in which the M_s temperature for athermal martensite is below the knee of the TTT curve [6]. Cooling curve 4 represents an overall transformation which starts as an athermal one and after holding at a temperature below the M_s and below the knee of the curve becomes isothermal in character. Curve 5 shows a transformation which starts as an anisothermal one, becomes athermal below M_s, and when held at a temperature below M_s and the knee of the curve becomes isothermal in character. Curve 6 represents a transformation which begins anisothermally and becomes isothermal on holding at a temperature above M_s. Finally, curve 7 represents an isothermal martensitic transformation. After holding at this temperature an athermal reaction may entail on quenching below M_s, depending on how far the transformation has progressed. These various sequences are summarized in Table II.

Table II. Possible Martensitic Transformation Sequences

Isothermal				
Athermal	→	Isothermal		
Anisothermal	→	Isothermal		
Athermal	→	Anisothermal	→	Isothermal
Anisothermal	→	Athermal	→	Isothermal
“Mixed Athermal and Anisothermal”			→	Isothermal

It should be pointed out that the anisothermal and isothermal reactions are really the same, both being thermally activated martensitic transformations. The only difference is whether they occur during cooling (anisothermal) or during holding at a fixed temperature (isothermal).

Discussion of the Difference Between Thermally Activated and Non-thermally Activated (athermal) Martensite

In Martensite which forms athermally, thermal energy alone is insufficient to initiate the transformation. Whatever the mechanism of the initiation of the transformation is, it cannot proceed by thermally induced fluctuations. The athermal transformation is initiated at specific sites only after a large enough chemical driving force is generated by cooling to a large enough degree below the equilibrium phase transformation temperature. This thermodynamic driving force must overcome the elastic (plastic) energy which is in opposition to the initiation at specific sites at and below M_s.

Thermal activation implies statistical probability, meaning the same site will not always be the first one to initiate the process. This is unlike some of the thermoelastic martensites where the same site has been shown to repeatedly initiate the process [7]. In thermoelastics, the site with the lowest barrier always is the first one to initiate the transformation, unlike thermally activated processes in which statistical probability considerations via the Boltzmann equation play a role in determining the time and site of the initial formation of the new phase.

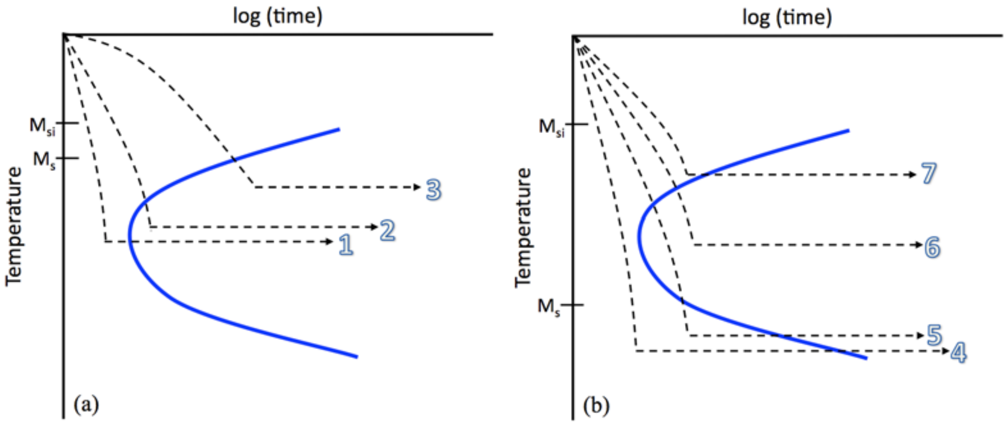

Figure 3. Schematic of the possible sequence of different martensitic transformations with (a) M_s above and (b) below the nose of the TTT Curve.

Thermoelastic martensites are athermal, since they need a larger driving force to proceed after initiation. This driving force can be supplied by lowering the temperature (and hence increasing the chemical thermodynamic driving force) or by supplying a stress to the sample. Since thermoelastic martensitic transformations are not initiated or grown by a thermally activated process, the term *thermo* in thermoelastic signifies temperature and is not short for thermally activated. Thermal in athermal and thermo in thermoelastic means that a temperature change is needed to either initiate new (*athermal* Martensite) or grow existing (*thermoelastic* Martensite) Martensite plates.

Rapid Anisothermal Transformations

If the C-curve for a thermally activated martensitic transformation intersects the temperature axis of the TTT diagram, a rapid quench may not suppress the transformation (See Figure 4). The transformation will appear to be an athermal one since it occurs rapidly without any apparent incubation time. Such a transformation could be called a “pseudo-athermal” transformation. One way to distinguish this kind of transformation from a truly athermal transformation is to hold the sample at the temperature at which the transformation was first observed. If it does not proceed with time it is truly an athermal transformation. If however the transformation continues over an extended period of time it is seen to be thermally activated and hence it started as an anisothermal transformation.

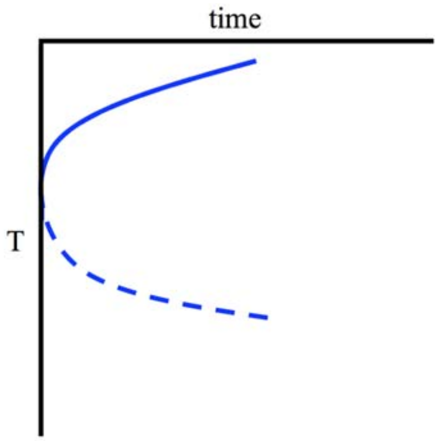

Figure 4. Schematic of a TTT Curve intersecting the temperature axis.

Summary

- Since isothermal martensite is the term used to describe thermally activated martensites, we believe that the term isothermal martensite should be replaced with the more descriptive term, thermally activated martensite, or TAM.
- We have given an overview of the terminology in use for the several types of martensites.
- We have discussed the initiation and growth processes of martensitic transformations as possibly being activated by thermal fluctuations.
- We have delineated the possible sequence of processes that could occur in martensite forming systems.

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