Step-wise stress-free martensitic transformation in the NiTi system

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Introduction

The martensitic transformation in NiTi system is a well known first order diffusionless transformation. The growth of a thermoelastic martensitic particle, following the thermodynamic analysis of Olson and Cohen(1), is intrinsecally dependent upon both shape and dimensions of the martensite plate. As the martensitic transformation evolves trough a mechanism of nucleation and growth which leads to martensitic particles with the same shape but progressively decreasing dimensions, a spread in the equilibrium temperatures can be expected and, as a consequence, both mechanical and thermodynamic properties connected with the transformation can show a step-wise character.
Step-wise recovery due to martensite-parent phase transformation has till now been shown to set in while investigating, under applied stress,the thermal recovery of stress-induced martensite in NiTi alloys(2).
The step-wise features of thermally induced parent-phase to martensite transformation and its connection with a fractal model have been shown in Fe alloys(3).Similar evidence in NiTi alloys being lacking,investigations have been here undertaken:in presence of a step-wise progression,the kinetics of the heat release during the transformation is expected to appear discontinuously.
As far as the step-wise character of the reverse martensitic transformation is concerned,another kind of step-wise evolution,thermally stimulated and macroscopically detectable, is here reported.

Experimental

Differential Scanning Calorimetry (DSC) has been adopted to evidence the intermittent heat flow released/absorbed during complete cycles of M ⇌ P transformations.
DSC scans have been performed on a Dupont 1090-910 DSC equipment provided with a mechanical cooling accessory,in the temperature range -80C - +120C, on several nearly equiatomic NiTi alloys.
Slow heating/cooling rates (≤ 0.5 C/min) were adopted to investigate the step-wise progression of martensite transformation.
The procedure followed to induce the stimulated step-wise evolution in the reverse M - P transformation relies upon Incomplete Cycles on Heating (ICH) performed at normal heating/cooling rate (10C/min),followed at last by a complete heating to the parent phase.
The conditions adopted to perform a typical sequence of ICH cycles, exemplified in fig.1,are as follows :
-the start temperature of each ICH cycle is below M_f;
-the highest heating temperature T_H never reaches the A_{peak} A_f;
-T_H is progressively lower during repeated ICHs, with

$$A_s < \dots < T_{H+1} < T_H \quad \dots < A_{peak} < A_f$$

This procedure has been applied on specimens previously stabilized to prevent transformation anomalies.

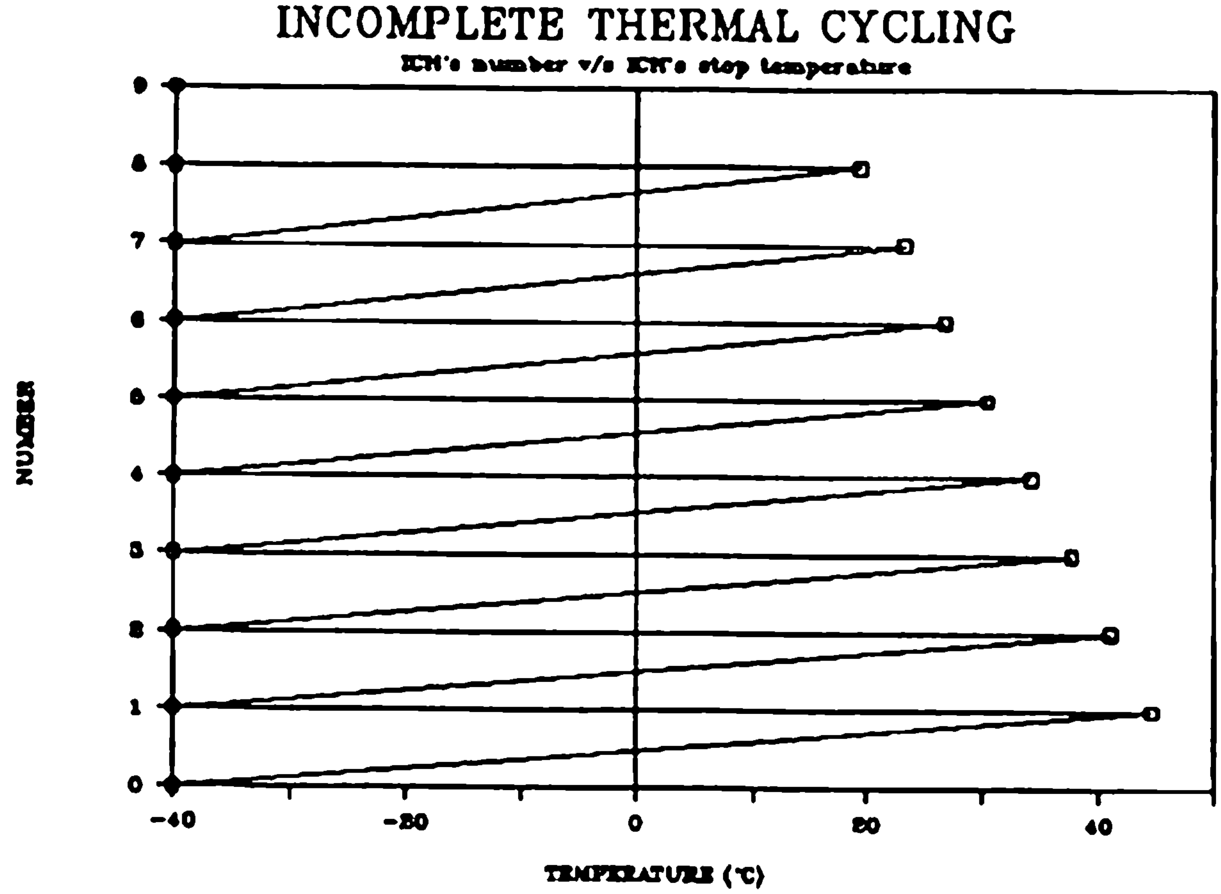

Fig.1 : A typical sequence of 8 ICHs.

Results

Step-wise stress-free M = P transformation

Fig.2 shows a typical heating/cooling scan performed at slow rate (0.5 C/min). As it can be seen,on the whole,the main peak shows an asymmmetry which always appear on the same side on the temperature scale.The main peak looks as the convolution of several lower peaks,as suggested by the smaller peaks and dips present on the main peak.
A critical examination of the experimental results affords to state:
-the asymmetry of the main peak is not due to the experimental procedure; on the contrary it supports the idea the transformation proceeds step by step, each related to a packet of martensite particles.The ranking of martensite packets appearing on cooling follows a reverse ranking on heating.
-the dips and the smaller peaks, superposed on the main one, exceed the experimental noise;
-the intermittent heat flow can be detected quite generally, provided a slow heating/cooling rate is adopted.

Stimulated step-wise martensite to austenite reversible transformation

Evidence is here given of a "memory" effect, thermally induced and reversible in NiTi alloys, which appears as a stimulated evolution in the martensite-parent phase transformation. The number of steps and their onset temperatures can be "memorized" by means of the procedure above described.

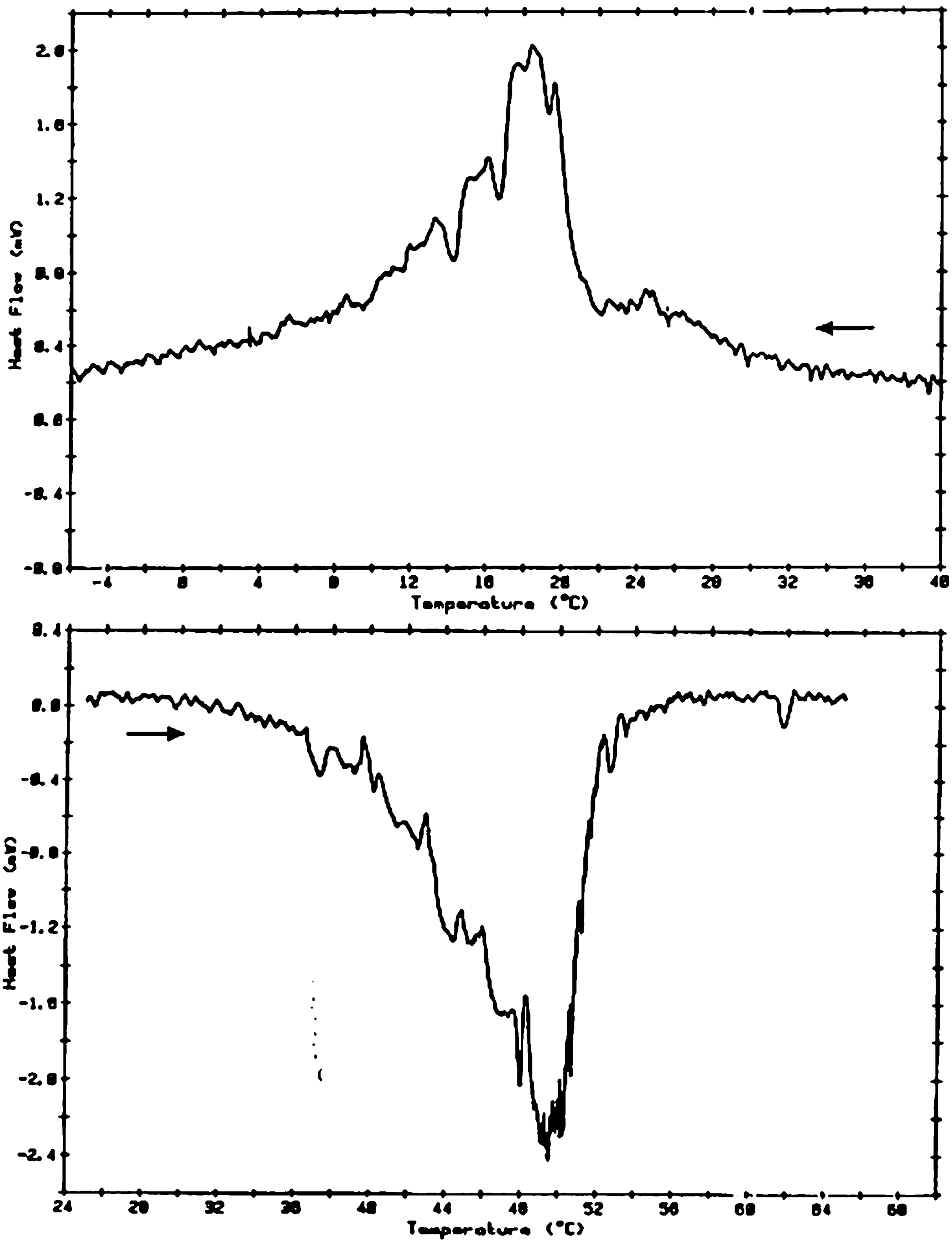

Fig.2 : DSC scans, on cooling and on heating, on a NiTi alloy at a rate of 0.5 C/min.

Fig.3 shows schematically the sequence of calorimetric runs required to induce and evidence the stimulated "step-wise martensite to austenite reversible transformation" (SMART) on a NiTi specimen. Curves (a) and (b) are referred to a complete heating/cooling cycle (in (b) the high temperature peak is due to the R-phase transformation, which is of no relevance on SMART). Curve (c) shows an incomplete cycle on heating (ICH) up to T* (A_s < T* < A_{peak}). SMART ensues from this essential stage, during the next heating to parent phase. As

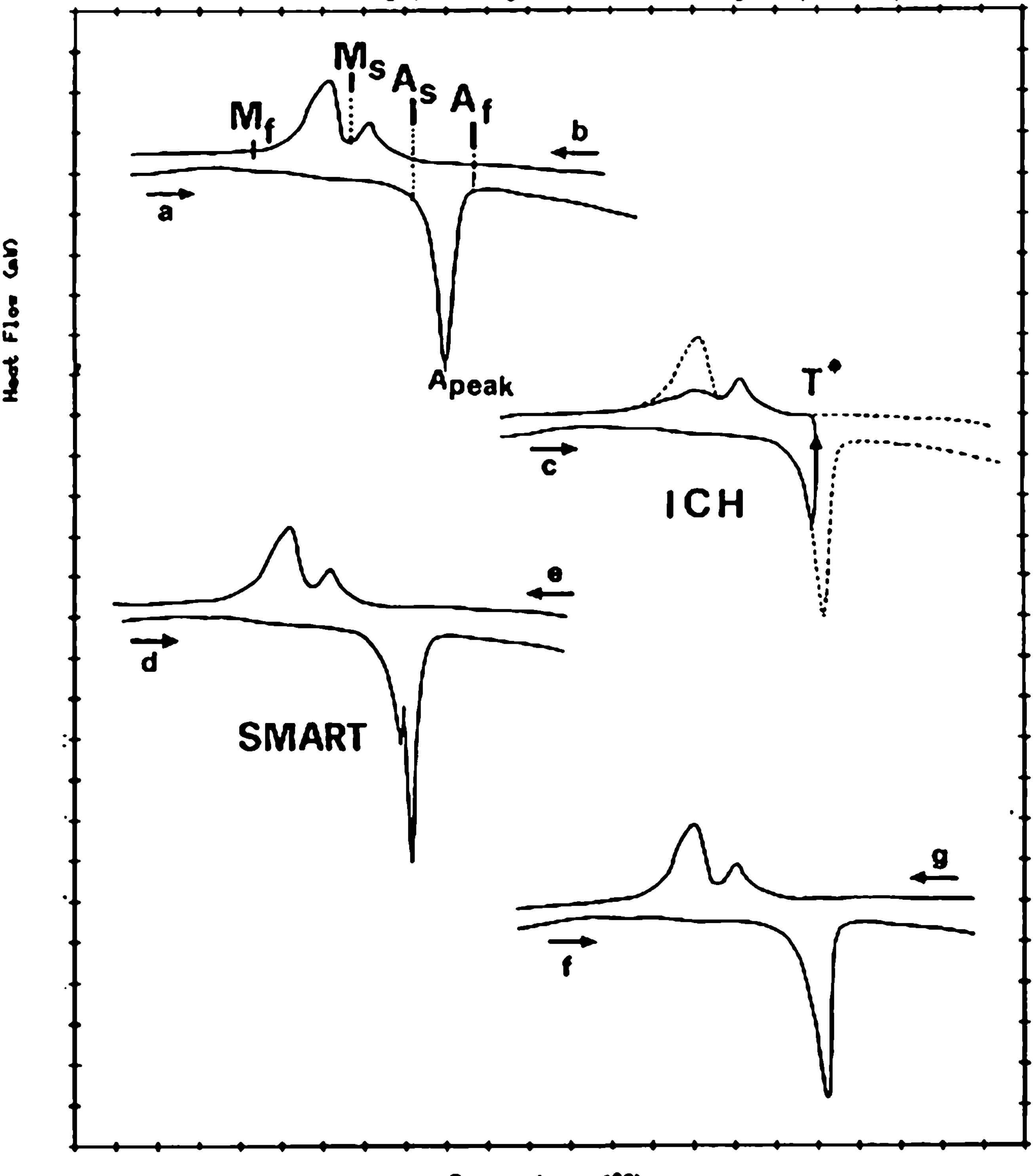

Fig.3 : Sketch of the sequence of calorimetric scans required to induce the stimulated SMART.Curves c), g) and f) are shifted on the temperature scale.

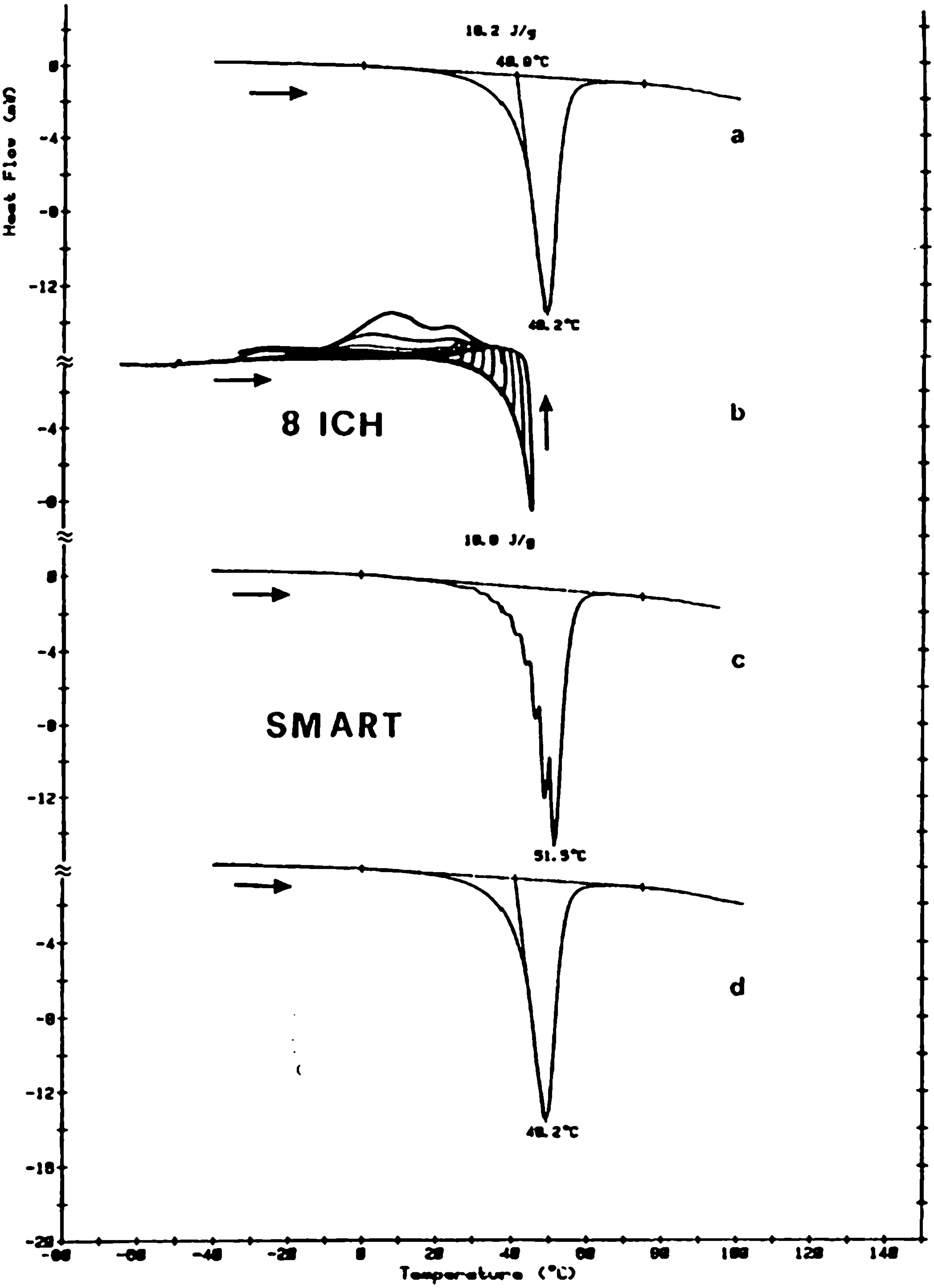

Fig.4 : SMART induced through 8 ICHs in a NiTi specimen according to the data given in Table 1. a) and d) are the heating scans performed respectively before and after SMART.

a matter of fact, the next calorimetric run on heating (d), exhibits a step-wise character: the heat flow associated with the H-P transformation has a sudden drop near T*. It is to be pointed out that the next cooling (e) is unchanged in comparison with (b) and the subsequent heating (f) shows the reversibility of the SHART: curve (f) identifies with (a).
Several repeated ICHs with $A_s<\ldots<T^*_{H+1}<T^*_H<\ldots<A_{peak}$ (i=0,1,2,...N) induce in the next complete heating run an heat flow with N peaks shifted each other of $\Delta T \cong T^*_H - T^*_{H+1}$. Table 1 shows the temperatures reached in a typical sequence of ICHs and the temperatures of the stationary points of the SMART thermogram; in fig.4b) the corresponding plots of DSC scans are given, followed by SMART on the next heating scan (fig.4c).

Table 1

ICH's	T*	T_{min}	T_{peak}
1	45.3	50.3	51.5
	(2.4)	(2.8)	(2.5)
2	42.9	47.5	49.0
	(2.4)	(2.7)	(2.6)
3	40.5	44.8	46.4
	(2.4)	(2.8)	(2.4)
4	38.1	42.0	44.0
	(2.7)	(3.0)	(2.7)
5	35.4	39.0	41.3
	(2.7)	(3.0)	(2.7)
6	32.7	36.0	38.6
	(2.7)	(3.0)	(2.8)
7	30.0	33.0	35.8
	(2.8)	(3.0)	(3.0)
8	27.2	30.0	32.8

Table 1 : Arrest temperature T* as a function of the ICH number. Temperatures corresponding to the stationary values of SMART are also given.In parenthesis the increments between two corresponding temperatures, given in sequence, are also quoted.

Discussion

Step-wise stress free transformation

Following the fractal model advanced by Hornbogen(3) to explain the martensitic microstructures,the enthalpy change of the whole transformation can be seen as the build up of several contributions corresponding to dimensionally decreasing/ increasing martensite particles,with selfsimilar features, appearing/disappearing with temperature.Details are given in (4).

Stimulated SMART

SMART is obtained only by ICH procedure : a similar sequence of incomplete cycles on cooling does not produce a SMART in the following complete cooling.
This points out the intrinsic difference between martensite and parent phase. SMART has moreover here been obtained at a standard scan rate (10°C/min) and

does not seem to require slower rates, as needed to evidence the step-wise features of martensitic transformation both on cooling and on heating.
Both above experimental findings suggest that SMART does not enhance the intrinsic step-wise character of the martensitic transformation,as slow rate scans do. On the contrary this step-wise feature is extrinsic to the freedom that SMART offers in the choice of both the temperatures at which peaks set in and the temperature shift within peaks.The absence of SMART as a consequence of incomplete cycles on cooling agrees with this view.
Is is to be pointed out that SMART can be induced in NiTi specimens regardless their thermal stability.It is well known that incomplete thermal cycling on unstabilized specimens induces partial stabilization of martensite and,hence, transformation anomalies in the next complete run, both on cooling and on heating.SMART was induced also in unstabilized specimens,but in that case two distinct processes occur: one irreversible, which increases the dislocation density due to incomplete thermal cycling; the other reversible, which introduces removable kinetic barriers.In NiTi specimens where a high dislocation density has already been introduced by thermal cycling and/or by alternative procedure(5),ICH procedure induces SMART only.
SMART looks as a characteristic feature of martensite:it is then tempting to attribute it to martensite variants which accomodate progressively on cooling to full martensite.Since 24 variants can be accomodated,it looks difficult to be able to establish the same number of peaks,currently limited by experimental resolution.At the light of present investigations it cannot be inferred if and to what extent variants are implied.

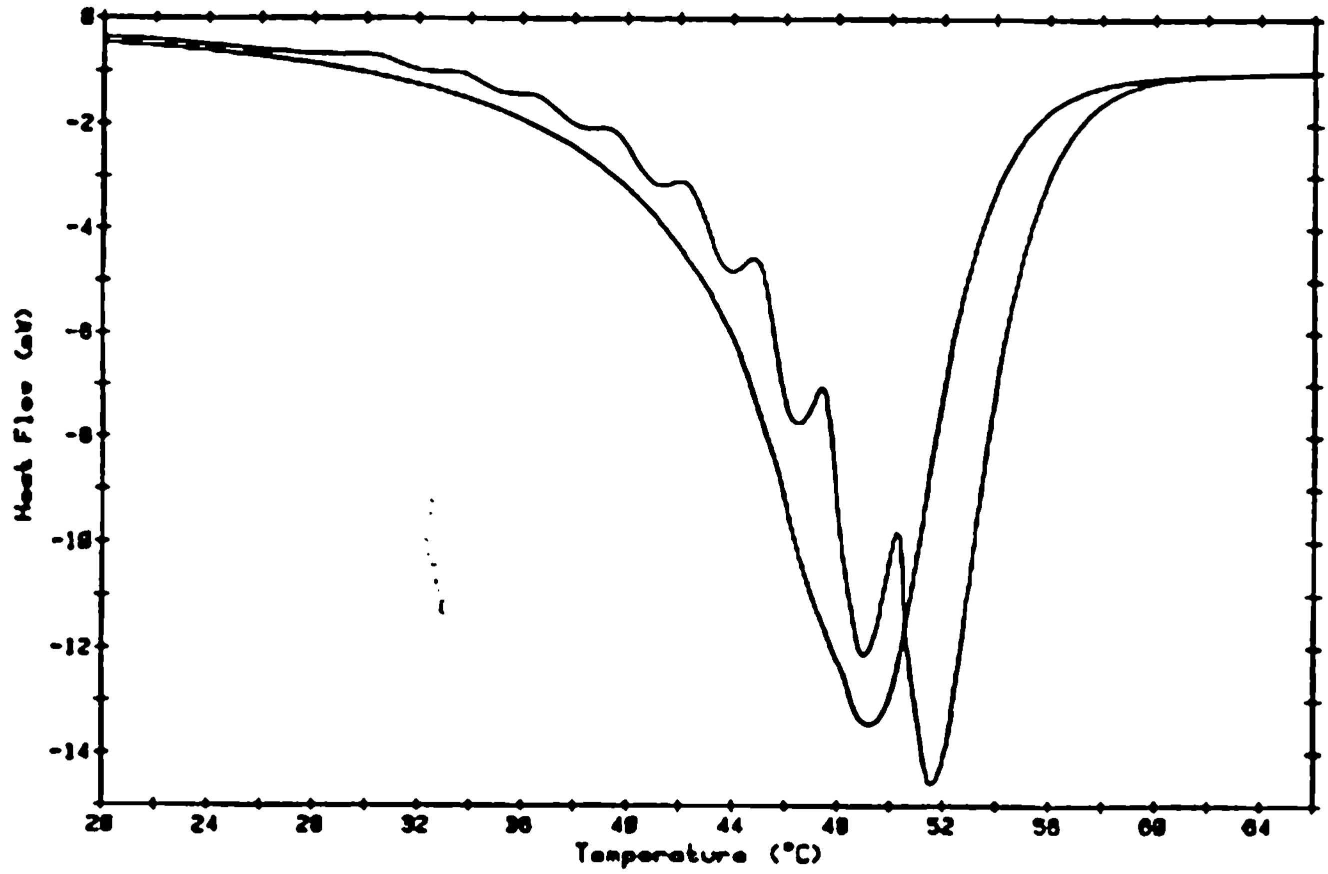

Fig.5 : Thermal scan before SMART (Fig.4a) superposed to the thermal scan showing SMART (Fig.4c).

The most reasonable hypothesis to explain SMART seems rely upon the come into being of kinetic barriers at boundaries between martensite and parent phase, during the ICH procedure.
"Memory" of the barriers at the temperature T_H* last during the following ICHs, which in sequence reach a lower and lower temperature. Memory is lost whenever heating is performed to parent-phase as in the last heating cycle which follows ICH.
As a matter of fact the DSC run on heating which evidence SMART is shifted to higher temperatures in comparison to a previous complete heating scan,free from ICH procedure, as shown in fig.5. Kinetic barriers,built up at each ICH step,require an overheating temperature than usual to be overcome.

Conclusions

At the light of present investigations it can be concluded:
-The step-wise progression of the martensitic transformation both direct and reverse, in NiTi alloys, is clearly related to a fragmentation process.The enthalpy change, derived(4) following Hornbogen fractal model of fragmentation, has a trend in agreement with experimental results.
Only microstructural investigations directed to determine shape and kinetics of martensite plates could however discriminate between fractal and non-fractal microstructures.
-On the contrary, in the same system, the stimulated step-wise reverse martensite transformation (SMART) does not enhance the intrinsic step-wise character of stress-free martensite, but it looks extrinsic. Experimental findings suggest it rises from removable kinetic barriers, built up, "saved" and "stored" in the specimen by the adopted ICH procedure and "erased" by a full reversion to the parent phase.

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