Calorimetry and Fractal Analysis of Stepwise Martensitic Transformation of NiTi Alloys

G. AIROLDI^{1,2)} and G. RIVA²⁾

¹⁾ Dipartimento di Fisica, Università Degli Studi di Milano, Via Celoria 16, 20133 Milano, Italy.

²⁾ ITM-CNR, Via Bassini 15, 20133 Milano, Italy.

(Received on August 25, 1988; accepted in the final form on December 20, 1988)

The stepwise character of the thermoelastic martensitic transformation in NiTi alloys is investigated in terms of the enthalpy changes connected with the transformation. Differential scanning calorimetry has been adopted to evidence the discontinuous heat flow developed during both the direct and reverse martensitic transformation. The results are examined at the light of a simplified fractal model advanced to describe the self-similarity of martensitic microstructures.

KEY WORDS: martensitic transformation; shape memory; NiTi alloys; fractal; enthalpy; calorimetry.

1. Introduction

The stepwise character of martensitic transformations has been suggested by Hornbogen¹⁾ to follow a fractal hierarchy and supported by experimental findings related to lenticular martensite in iron alloys.^{2,3)} The recovery of stress-induced martensite in a NiTi alloy has recently been shown⁴⁾ to exhibit a stepwise character.

Widespread evidence of the fractal nature of the thermoelastic martensitic transformations is, however, still lacking. With the aim to enlighten this point, the thermal martensitic transformation of NiTi alloys is examined in the present study under proper experimental conditions to detect the natural intrinsic stepwise features of the martensitic transformation.

2. Experimental

In accordance to the hypothesis that the stress-free thermally induced martensitic transformation follows a fractal hierarchy, the enthalpy change associated with the elemental fragmentation is expected to bear a close resemblance to the fractal behaviour. Differential scanning calorimetry (DSC) was used, in the same way as previously specified⁵⁻⁷⁾: a very slow heating and cooling rate ($\leq 0.5^\circ\text{C}/\text{min}$) is required to detect the stepwise character of the transformation. All the NiTi specimens here examined correspond to a nominal equiatomic start composition: different final thermal treatments (ageing at 400 or 500°C) were used.

3. Results

Typical DSC scans which followed the direct parent phase(*P*)-martensite(*M*) and the reverse *M*-*P* transformation, were obtained at a heating and cooling rate of $10^\circ\text{C}/\text{min}$ as plotted in Fig. 1. DSC scans of the same specimen, at a heating or cooling rate of

$0.5^\circ\text{C}/\text{min}$, are given in Fig. 2 to show the detail of what is going on. First of all, the heat flow peaks show on the whole a clear asymmetrical broadening at the low temperature side. While examining the scans on cooling in more detail, after a small smeared out bump connected with an incipient *R*-phase transformation,^{5,6)} which has no relevance in the present case, the heat flow connected with the *P*-*M* enthalpy change in transformation appears in a discontinuous way, with small peaks and dips which significantly modify the original main bulk peak. The same discrete character of the heat flow appears on heating. The present results appear intrinsic and indicative of an underlying mechanism, provided the DSC scans be performed at a slow rate. Fig. 3 shows another typical scan obtained at a rate of $0.2^\circ\text{C}/\text{min}$.

4. Discussion

The above experimental findings seem suitable to fit a fractal model put forward by Hornbogen¹⁾ to explain the microstructures which evolve in martensitic transformations of iron alloys.

This is supported by:

(1) the intermittent heat flow detected during DSC scans through the whole transformation temperature range suggests that the main heat flow peak is the convolution of several smaller heat flow peaks, each corresponding to the contribution from specific martensite packets of fragmentation;

(2) the rank of the elemental heat flow peaks corresponds to the rank of fractal microstructures evolved;

(3) the asymmetrical broadening of the main heat flow peaks proves the sequence of martensite packets, which successively appear on cooling and disappear with a reverse sequence order on heating. If this asymmetry was to be attributed so instrumental inertia or thermal gradients within the specimen, it would appear with the same sequence both on cooling

Sample: NITI G F1 X 500+WQ

Size: 81 MG

Rate: 10 C/MIN

Program: Interactive DSC V3.0

DSC

Date: 11-Mar-88 Time: 14:07:41

File: NITIGF1X7C.01 ITM CNR 39

Operator: GR

Plotted: 23-Sep-88 16:25:55

(a)

Sample: NITI G F1 X 500+WQ

Size: 81 MG

Rate: 10 C/MIN

Program: Interactive DSC V3.0

DSC

Date: 11-Mar-88 Time: 13:44:44

File: NITIGF1X6H.01 ITM CNR 39

Operator: GR

Plotted: 23-Sep-88 16:40:45

(b)

Fig. 1. DSC scans at a rate of 10°C/min, for a NiTi specimen, aged at 500°C: (a) on cooling; (b) on heating.

Fig. 2. DSC scans at a rate of 0.5°C/min: (a) on cooling; (b) on heating.
 The specimen is the same as in Fig. 1.

Fig. 3. DSC scan at a heating rate of 0.2°C/min for a NiTi specimen aged at 400°C.

and on heating⁸); and

(4) a simplified fractal model as will be described in the following.

5. Simplified Fractal Model

The free energy change involved in the formation of a martensite particle (oblate-spheroidal in shape) of radius r and semithickness c is given⁹) by

$$\Delta G = 4/3\pi r^2 c (\Delta G_{ch} + \Delta G_{el}) + 2\pi r^2 \sigma, \quad (1)$$

where, ΔG_{ch} , ΔG_{el} : the chemical free energy and the elastic free energy per unit volume of the particle, respectively
 σ : the interfacial energy per unit surface of the particle.

In the case of NiTi alloys the self-similarity features of the martensite variants^{1,10}) in progressive evolution during P - M transformation look quite similar to the geometrical shape of the "Sierpinski gasket" as proposed by Mandelbrot¹¹) to describe fractal structures.

A simplified bidimensional martensite particle growing with an equilateral triangular shape as in the Sierpinski gasket model entails a free energy change given by

$$\Delta G = A(\Delta G_{ch} + \Delta G_{el}) + P\sigma, \quad (2)$$

where, $A = (\sqrt{3}/2)L^2$: the surface

$P = 3L$: the perimeter of a specific particle.
 The free energy changes ΔG_{ch} and ΔG_{el} are referred

to the unit surface and the interfacial energy is referred to the unit length.

The growth of the particle will be stopped whenever $d\Delta G/dL = 0$ which corresponds to:

$$\sqrt{3}L(\Delta G_{ch} + \Delta G_{el}) + 3\sigma = 0. \quad (3)$$

At the stage of X -fragmentation, L has a length L_X , therefore

$$\Delta G_{ch}^X = -(\sqrt{3}/L_X)\sigma - \Delta G_{el}. \quad (4)$$

As a reasonable hypothesis ΔG_{ch} is given by

$$\Delta G_{ch}^{(X)} = \Delta H^{(X)} - T_X \Delta S \quad (5)$$

around T_X at which the X -fragmentation will set in with $T_{X+1} < T_X$ ($X = 0, 1, \dots, N$) in cooling.

By equating the above expressions for the free chemical energy change, it leads to

$$\Delta H^{(X)} = T_X \Delta S - (\sqrt{3}/L_X)\sigma - \Delta G_{el}, \quad (6)$$

which gives the enthalpy change per unit surface on the formation of a single packet corresponding to the X -fragmentation element.

By defining N_X as the number of elements of surface A_X associated to the X -fragmentation, the total enthalpy change connected with the X -fragmentation will be

$$\Delta H(X) = N_X \Delta H^{(X)} A_X. \quad (7)$$

For the case of the Sierpinski gasket with an initial dimension L_0 ,

$$N_X = 3^{X-1}; \quad L_X = L_0(1/2)^X, \quad \dots\dots\dots(8)$$

and

$$\Delta H(X) = L_0^2/2 \sqrt{3} (3/4)^X \{T_X \Delta S - (\sqrt{3} \sigma/L_0)2^X - \Delta G_{el}\}. \quad \dots\dots\dots(9)$$

The enthalpy change $\Delta H(X)$ connected with the whole X -fragmentation clearly decreases on increasing X .

6. Conclusions

The present experimental findings suggest the step-wise nature of the thermoelastic stress-free martensitic transformation in NiTi alloys. The experimental enthalpy change evolution, here detected, agrees with the simplified fractal model of fragmentation: the heat flow related to the enthalpy change shows a composite peak due to the convolution of several contributions which decrease with cooling and increase with heating. More extensive micrographic observations related to the kinetics of the transformation would be advisable to definitely assess or contrast the fractal geometry progression of the transformation.

Acknowledgements

Thanks are due to the "Centro di Studio dei Processi Elettrodici CNR" for the access to research facilities. The research has been partially supported by M.P.I. 60 % funds.

REFERENCES

- 1) E. Hornbogen: *Z. Metallkd.*, **78** (1987), 352.
- 2) Unpublished results of N. Host cited in Ref. 1).
- 3) C. M. Wayman: *Physical Metallurgy*, R. W. Cahn and P. Haasen, eds., North-Holland, Amsterdam, (1983), 1031.
- 4) R. Lohman: *Z. Metallkd.*, **78** (1987), 355.
- 5) G. Airoidi and B. Rivolta: *Phase Transformations '87*, G. W. Lorimer, ed., Inst. Metals Publ., London, (1988), 74.
- 6) G. Airoidi and B. Rivolta: *Phys. Scr.*, **37** (1988), 891.
- 7) G. Airoidi, G. Riva and B. Rivolta: *Proc. MRS Int. Meeting on Advanced Materials*, Mater. Res. Soc., Pittsburgh, (1989), in press.
- 8) J. Kwarciak and H. Morawiec: *J. Mater. Sci.*, **23** (1988), 551.
- 9) G. B. Olson and M. Cohen: *Scr. metall.*, **9** (1975), 1247.
- 10) C. M. Wayman: *Proc. on Int. Conf. Mart. Transf. (ICOMAT-86, Nara)*, Japan Inst. Met., Sendai, (1987), 645.
- 11) B. B. Mandelbrot: *The Fractal Geometry of Nature*, W. H. Freeman and Co., New York, (1987).