ACOUSTIC EMISSION CHARACTERIZATION OF THE MARTENSITIC PHASE
TRANSFORMATION IN NiTi

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INTRODUCTION

Equiatomic NiTi alloys possess the unusual property of a shape memory effect (SME) [1,2]. They have recently begun to attract renewed interest because of the emergence of increasing numbers of industrial applications. The origin of the effect is based upon a stress induced martensitic transformation in material held just above the $M_s$ temperature (the temperature at which martensite starts to form on cooling with no stress applied). The martensitic transformation occurs by a diffusionless shear mechanism involving the cooperative movement of groups of atoms. It is believed to be accompanied by release of elastic energy and is thus a source of acoustic emission. Early research indicated the martensitic transformation involved a change of crystal structure from B2 (CsCl) to B19 (monoclinic) by a diffusionless shear/dilation strain [3]. More recent work indicates the possibility of other transformations of the B2 state before the martensite forms [4-6]. These "pre-martensitic" phenomena have been observed by electron diffraction and electrical resistivity in NiTiFe alloys where the presence of iron depresses $M_s$ exposing the pre-martensitic behavior more clearly. The sequence of transformation events (on cooling in the NiTiFe alloy) is believed to be: B2 + incommensurate (distorted cubic) phase + commensurate (rhombohedral) phase + martensitic (B19, monoclinic) phase.

To determine the transformation sequence in the NiTi alloy itself is more difficult because of the truncation of pre-martensitic effects by the martensitic transformation. Techniques are required to precisely detect the temperatures at which the various transformations occur. The commonly used technique of electron microscopy is not suitable for this because image stresses associated with the surfaces of thin foils alters the stress assisted martensitic transformation. Instead, in this investigation the use of acoustic emission [7] to monitor and characterize the transformation in bulk samples is explored. Furthermore, the aim was to determine the critical points and the kinetic parameters of the transformation in NiTi, as well as to corroborate the acoustic emission results with electrical resistance and optical microscopy examination.
Experimental

A Ti 50 at% Ni alloy was prepared by arc melting. Samples 4.6 mm thick and 8.1 mm in diameter were subsequently homogenized 24 hours at 850°C under an argon atmosphere. Prior to the commencement of tests, samples were further annealed at 850°C for 24 hours and rapidly cooled by quenching into water.

Heating/cooling cycle experiments were performed in the apparatus shown in Fig. 1. The sample was held against the acoustic emission transducer with a constant force. No coupling medium was used, reducing detection sensitivity somewhat but eliminating variations in coupling efficiency with temperature. The sample and transducer were housed in the center of a small 50 watt furnace within a cryostat. The furnace allowed the sample temperature to be continuously increased to 190°C. Cooling from ambient was achieved by continuous variation of mixtures of dry ice/alcohol/liquid nitrogen. This enabled temperatures as low as -196°C to be achieved. Electrical resistivity and temperature were simultaneously measured with the acoustic emission. For some cycles, the acoustic emission transducer was replaced with an ultrasonic device for measuring ultrasonic velocity.
The acoustic emission was detected with a 150 kHz resonant transducer, amplified 60 dB in a pre-amplifier and analyzed in a microcomputer based acoustic emission apparatus manufactured by the Physical Acoustics Corporation*, Fig. 2. For the experiments reported here, only the number of acoustic emissions whose amplitude exceeded a preset threshold was used. This information together with electrical resistivity and temperature were simultaneously plotted through the entire thermal cycle.

RESULTS AND INTERPRETATION

Optical Metallography

Optical metallography has been used to characterize the microstructures of high (B2) and low (M) temperature phases. The high temperature phase had a roughly equaxed grain size of 15 μm. Even though the sample had been extensively homogenized, dendritic coring still persisted at a Ti₂Ni phase was present at the grain boundaries. The low temperature microstructure contained colonies of martensite, Fig. 3. The feathery pattern of the laths arises from coplanar martensite laths, nucleated from a common plane, protruding into untransformed high temperature phase.

*Disclaimer
The use of this instrument should not be interpreted as an endorsement of
Acoustic Emission

Acoustic emission could be detected both on cooling and heating (provided the sample had been cooled to below $M_s$). The dependence of the emission upon temperature is shown in Fig. 4. As a sample was cooled from 20°C (B2 phase) sporadic acoustic emission events were detected. At -0°C, the rate of emission sharply increased and reached a maximum at
-30°C. Further cooling resulted in continued emission but at a gradually decreasing rate. At the higher temperatures, the emission was athermal, that is no emission was detected once the sample had reached its new lower temperature. At the lower end of the temperature range, isothermal emission was observed, i.e., the emission persisted while the temperature was constant, eventually disappearing after several hours.

Upon heating from -75°C no emission was observed until the temperature had reached 70°C. A few sporadic events were detected over the next 15°C. At 85°C, the emission rate increased sharply and went through a maximum at 100°C before ceasing above 150°C. More acoustic emission events accompanied cooling than heating when a sample was cooled below M_s and above A_s, respectively.

Figure 5 exhibits a comparison between the acoustic activity and electrical resistance variation during the martensitic transformation. It was found that the acoustic emission detected at low threshold voltage levels can be very sensitive for the precise determination of the critical transformation points.

DISCUSSION

The volume fraction of the martensitic phase, f(M), during the cooling semicycle (Fig. 6) was determined by assuming that f(M) is proportional to the ratio of cumulative events at each temperature with respect to the total number of cumulative events at a temperature where the reaction ceased to progress. f(M) = α(M_s - T) in the temperature range of M_f < T < M_s. The proportionality constant α was found to be 0.013 for the martensitic transformation and 0.036 for the antimerensitic reaction. The behavior of the transformation (Figs. 4 and 6) was found to be mostly athermal except at the lowest temperatures, where the transformation assumes an isothermal character.

Figure 4 shows the acoustic activity during a complete thermal cycle through the martensitic phase transformation range in NiTi. The data enabled determination of the critical temperatures. For this specific NiTi alloy the following have been found: M_s = 0°C, M_f = 103°C (completion of the martensitic transformation), A_s = 85°C and A_f = 150°C (completion of the antimerensitic transformation, to the cubic B_2 phase). The martensitic transformation hysteresis, between cooling and heating was found to be ΔT = 135°C (see Fig. 6).

The thermoelastic free energy balance during the B2→M phase change, following Salzbrenner and Cohen [8] can be written in the form:

$$\Delta G_{B2\rightarrow M} = \tau V_m \sigma^* - \Delta G_{el}$$

where V_m is the volume of the region transformed, τ the shear stress required to propagate the transformation interface, σ^* the transformation strain and ΔG_{el} the elastic strain energy set up by the transformation. The strain energy of the transformation is V_mσ^* so that

$$\Delta G_{B2\rightarrow M} = \tau V_m \sigma^* - V_m \sigma^*$$

$$= -(c + \tau_0) V_m \sigma^*$$
where \( \sigma \) is the elastic stress in the material (B2) surrounding the transformed region. This expression indicates that the elastic energy, i.e., the acoustic emission energy is proportional to the volume of material that transforms. Then, it is reasonable to assume the rate of acoustic emission with respect to temperature is proportional to the rate of the transformation. From Fig. 6, we see that:

\[
\frac{\partial V_m}{\partial T} \bigg|_{B2\rightarrow M} = \alpha = 0.013 \quad \text{and} \quad \frac{\partial V_m}{\partial T} \bigg|_{M\rightarrow B2} = \alpha' = 0.036.
\]

These expressions are in agreement with the experimental results (Figs. 4 and 6) indicating that the driving force for the M\( \rightarrow \)B2 antimartensitic reaction is greater than that for the martensitic reaction (B2\( \rightarrow \)M), a fact borne out by experiment. Moreover, the large temperature hysteresis can be explained by the relatively higher configurational energy \( \Delta H_{\text{conf}} \) that remains stored in the martensitic phase [10,11].

Acoustic emission during a martensitic transformation arise from several distinct processes [9].

- The shape change (transformation strain).
- The interaction of the modulus change with pre-existing strain (both static and self-induced).
For small modulus differences between parent and martensitic phase, the dipole components of the acoustic source can be written [9]:
\[ \Delta \sigma(t) = C \beta V(t) \]
where \( C \) are the stiffness elastic constants of the parent phase, \( \beta \) the shape change (stress free transformation strain) and \( V(t) \) the volume of the region that transforms.

In a martensitic phase change, numerous discrete (localized) martensitic processes occur. Provided the transformations are abrupt (occur in microsecond times or less) then, a fraction at least will give rise to detectable signals. In the experiments reported here, a laser calibration technique [12] was used to determine the magnitude of the smallest detectable dipole. This was found to be \( 36 \times 10^{-6} \) Nm. Using a value of 180 GPa\(^{-2}\) as representative of the stiffness of the B2 phase the smallest detectable \( \beta V \) product of 200 \( (\mu m)^3 \) can be determined. Assuming a typical shape change strain of 0.05, the smallest detectable lath volume would be 4000 \( (\mu m)^3 \) equivalent to a 200 \( \mu m \) x 10 \( \mu m \) lath of 2 \( \mu m \) thickness, consistent with features observed metallographically.

If it is assumed that the number of acoustic emission events emitted during a transformation is proportional to the total volume transformed then acoustic emission can be used to estimate the critical transformation parameters such as \( M_s \), \( M_f \), \( A_s \) and \( A_f \). Fig. 4 shows the
result for a typical heating/cooling cycle. Upon heating martensite from -150°C the transformation to B2 begins first at the $A_s$ temperature of 85°C. The transformation rate suddenly increases, goes through a maximum and finishes at 150°C. The precise temperatures at which the first and last emission are observed is highly variable, probably reflecting the scatter in internal transformation nuclei. To obtain a better (in the sense of less scatter) estimate of the transformation temperatures, the approximately linear region near highest transformation rate is extrapolated to the 0 and 100% abscissas and $A_s$ and $A_f$ values of 85°C and 112°C determined. In a likewise manner the $M_s$ and $M_f$ values are obtained upon cooling from the B2 state.

The data shown in Figs. 4 and 6 indicates the existence of substantial hysteresis; that is the martensite and antimartensite transformations occur at different temperatures with a typical separation of 135°C. This hysteresis which is characteristic of a martensitic transformation arises from frictional work and plastic deformation (irreversible processes) that accompany the transformation on cooling. The transformation to martensite can be viewed as trade-off between a reduction in chemical free energy (configurational enthalpy) and an increase in elastic forces in and around the region undergoing transformation. At a given temperature, a balance exists between these
opposing forces that determines the fraction of material transformed. Reducing the temperature increases the driving force and allows the transformation to progress. Upon heating, the elimination of elastic strain drives the transformation against the decreasing chemical free energy. The path of the two transformations would be the same but for irreversible work, principally nonelastic deformation.

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References

Figure Captions

Fig. 1  Heating/cooling device.

Fig. 2  Block diagram of measuring system.

Fig. 3  Optical microscopy of NiTi at a) B2 phase (h, t, p) and b) martensitic phase (l, t, p).

Fig. 4  Cumulative events vs. temperature at virgin sample, where the gain = 89DB and the threshold voltage = 1V.

Fig. 5  Acoustic emission activity rate in comparing to resistance change vs. temperature.

Fig. 6  The complete thermal cycle of volume fraction of martensite, f(M) vs. temperature.
BLOCK DIAGRAM OF THE SYSTEM

Floppy Disk Storage

Chart Recorder

A.E. Rate of Resistance

Noise Threshold

40 dB Variable

Microcomputer-Based A.E. Recording System

Preampifier

(50-500 KHz)

Transducer

Voltmeter

Ohm Meter

Thermocouple

Sample (NiTi)
A. B2-STRUCTURE OF NiTi (HTP,) AFTER 850°C, 65h
(WATER QUENCH TO 20°C)

B. MARTENSITE STRUCTURE OF NiTi (LTP),
AFTER -78°C, 18h