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## Phase transformations in engineering materials

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### ABSTRACT

Phase transformations in engineering materials are inevitably related to mechanical behaviour and are often precursors to residual stress and distortion. Neutron scattering in general is a valuable tool for studying their effects, and pulsed neutrons are of special value, because of the inherently comprehensive crystallographic coverage they provide in each measurement. At the Manuel Lujan neutron scattering center several different research programs have addressed the relationships between phase transformation / mechanical behaviour and residual strains. Three disparate examples are presented; 1) Stress induced transformation in a NiTi shape memory alloy, 2) Cryogenically induced transformation in a quenched 5180 steel, and 3) Time resolved evolution of strain induced martensite in 304 stainless steel. In each case a brief description of the principle result will be discussed in the context of using neutrons for the measurement.

### 1. TRANSFORMATIONS IN ENGINEERING MATERIALS

One major focus of neutron diffraction (n.d.) is on the study of residual stress in heterogeneous materials. For example extensive n.d. measurements have been made on metal matrix ceramic composites, in which stresses are introduced because of differences in the coefficients of thermal expansion (CTE) of the constituents. However composites are also produced by incomplete or inhomogeneous transformations leading to both macro and micro stresses between different phases of the same starting material. These stresses impact not only the mechanical properties but also couple to the transformation kinetics.

One process in which transformations are of paramount importance is carburizing heat treatment. Carburizing of steel components is commonplace, especially in the automobile industry, to produce hard, compressively stressed surface layers for improved wear and fatigue performance. The effect is achieved by high temperature diffusion of carbon into the surface that lowers the martensite start temperature [M<sub>s</sub>] of a surface layer with respect to the interior. Then, on quenching, transformation of near surface austenite occurs after the interior and the concomitant volume dilation is resisted by the core, producing a compressive stress balanced by subsurface tension. Although the transformation kinetics are well understood, the stress distributions are hard to predict because of the superposition of the martensite / austenite microstresses on a macrostress associated with the case depth. Furthermore the magnitude of the stresses will depend on the degree of transformation induced plasticity which is discussed in section 4.

There are, of course, many techniques for studying phase transformations; two common ones are dilatometry, in which transformations are *inferred* from changes in bulk dimension, and X ray diffraction which probes surface transformations. However n.d. has advantages that supersede many conventional approaches. Phase transformations usually result from external stimuli such as load, pressure or temperature, so a technique for studying them should provide the stimulus without impeding the measurement. Also, in engineering, bulk behaviour is usually of importance, and techniques that focus on small or unrepresentative regions can be misleading with respect to bulk behavior. Obviously the penetration of neutrons addresses both of these criteria - with measurements in pressure cells and ovens being commonplace, as well as the implicit bulk sampling of specimens that are often measured in cubic centimeters.

### 2. VALUE OF PULSED NEUTRONS

Changes in diffraction patterns during transformations can be subtle, like small intensity changes resulting from twinning [1], or dramatic, with complete structure changes during diffusionless transformations. In either case, obtaining a complete diffraction pattern is valuable for two reasons. First, it facilitates the use of Rietveld techniques which simply quantify both volume fractions and lattice parameters of overlapping or minority phases. Second, if the textural state of the evolving phase is strong (as in the NiTi example below) reflections in some scattering geometries may be weak or even absent, but since all crystallographic orientations are probed simultaneously, other reflections will almost certainly be present in the spectrum. The following examples were selected to illustrate different aspects of phase transformations as they pertain to engineering

materials. In each case, a brief description of the problem and rationale for using neutrons is stated. This is followed by the principle result and its potential impact. In all examples the irradiated volume was in excess of  $1\text{cm}^3$ . Count times per measurement were greater than an hour for the NiTi and 5180 steel examples, and about 1 minute for the 304 stainless steel.

### 3. STRESS INDUCED MARTENSITE IN SUPERELASTIC NiTi

Shape memory and superelastic alloys have been extensively studied and commercialized as thermally activated actuators and spectacle frames, to name but two examples. This is despite the existence of basic questions concerning their crystallographic transformations, for example, what determines the mechanical hysteresis seen in superelastic alloys? One impediment to their study is the need to quantify bulk crystallographic performance (as distinct from the bulk *macroscopic* performance). Single crystal experiments using X-ray diffraction accurately describe the underlying transformations. But in polycrystals, grains which might transform at the surface, may be constrained by their neighbours in the bulk, and X ray measurements at free surfaces may be unrepresentative. The problem becomes even more complicated when phase mixtures or reinforcing phases are present, and the only way to get phase discrete bulk strain information is to use neutron diffraction.

NiTi alloys with near equiatomic composition are ordered intermetallics. They can exhibit either shape memory or superelastic behavior depending on composition. For superelastic NiTi, the austenitic (B2 cubic) phase, can deform during uniaxial loading by forming stress-induced martensite (B19 monoclinic). Upon unload, the martensite becomes unstable and transforms back to austenite, so that the strain is recovered; this phenomenon is known as superelasticity. As a precursor to studying a TiC reinforced NiTi alloy, we recorded neutron diffraction spectra during *in situ* compressive uniaxial loading on a NiTi cylinder (24mm long and 10mm in diameter). Diffraction patterns were recorded at discrete loads on loading and unloading between 0 MPa and -625 MPa. The maximum strain (including both transformation and elastic contributions) was 2.9%, which was completely recoverable on unloading. In Figure 1 a short section of the spectrum is shown, for which the scattering vector  $Q$  was parallel to the load. The reduction in intensity of the austenitic [100] reflection at  $\approx 3.0\text{\AA}$  is matched by the increasing martensitic [100] at  $\approx 2.86\text{\AA}$ . A Rietveld analysis, incorporating a texture approximation using a March-Dollase model, quantified the austenite / martensite ratio at various loads (Figure 2). The texture of both the nascent martensite and the ensuing texture in the decreasing austenite was extremely strong. Analysis of this texture is of considerable relevance in identifying the proclivity of grains with different orientations to the loading axis, to transform. A comprehensive texture analysis of the data, using spherical harmonics, has provided pole figure density distributions, in which the departure from random texture can be compared for any crystal orientation.

These measurements on the pure alloy provide a baseline for comparisons with reinforced NiTi, in which inert, elastic TiC particles are added to modify the mechanical properties. The resulting mismatch will result in; (i) allotropic and thermal expansion mismatches during heating or cooling, (ii) twinning mismatch upon deformation of martensite, and (iii) transformation mismatch upon deformation of austenite. Since the thermal and mechanical behavior of NiTi is very sensitive to stresses, these mismatches and the associated stresses are expected to influence strongly the composite mechanical behavior.

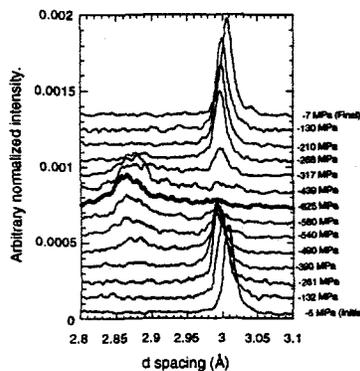


Fig. 1 Displaced spectra showing a short section of the NiTi spectra at various stresses. The shift to shorter d spacings results from the increasing elastic compressive strain. The data have been smoothed and displaced for clarity.

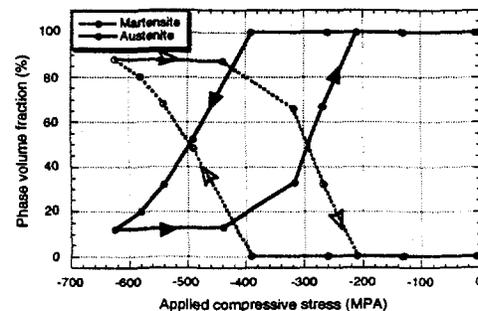


Fig 2. The relative intensities of the austenitic and martensitic diffraction patterns can be converted to the respective volume fractions of the two phases. Martensite starts to form at compressive loads greater than -400 MPa but on unload remains present until below -280 MPa.

#### 4. CRYOGENICALLY INDUCED TRANSFORMATION IN A 5180 STEEL

In carburizing treatments of steel, one aspect that is poorly quantified is transformation induced plasticity (TRIP). TRIP describes the irreversible deformation that can occur between phases during a transformation. For example, when an austenitic grain transforms in a martensitic matrix, its dilation, and thus volume mismatch, can be accommodated either by elastic or plastic strain. The respective contributions ultimately affect the microconstitutive behaviour of the mixture. However, distinguishing elastic and plastic microstrains in bulk specimens is notoriously difficult, and to date, most studies of its effects have been theoretical or computational[2]. In an attempt to address the problem we postulated that elastic strains might be measurable during a partial transformation provided that varying phase fractions could be controlled and held long enough to collect neutron diffraction data. In a conventional quench of a steel component, from temperatures typically above 700°C, the martensite to austenite transformation occurs in a few seconds, obviously much too quickly to be of relevance to a neutron measurement. Consequently we used cryogenic cooling as method to controllably alter the martensite to austenite ratio.

We examined a cylinder (50mm long, 10mm in diameter) of high carbon steel (5180) that, in its quenched room temperature state, contained 20 vol% retained austenite. By lowering its temperature between ambient and 100K it was possible to reduce the austenite fraction to a minimum of 10%. This type of cryo soak is often applied to carburized parts to transform near surface retained austenite. Diffraction patterns recorded at different temperatures were analyzed using a Rietveld refinement (Fm3m for the austenite and I4/mmm for the martensite) and the austenite phase fraction is shown as a function of temperature in figure 3. The irreversible transformation occurs between 220 and 150K i.e. between the dotted lines. However our interest concerned the possibility that changes in the phase fractions might alter the mean phase incompatibility. If this occurs, changes in the mean phase elastic strains might be seen by comparing initial and final lattice parameters (during cooling one has to contend with the CTE effect that complicates the interpretation).

In Figure 4 the austenite lattice parameter is shown for the cycle shown in figure 3. There is a clear difference between the final and initial austenitic lattice parameters. Comparison of the warming and cooling curves supports the assertion that the change occurs simultaneously with the transformation. If the difference were interpreted as an elastic strain it would suggest that the mean phase strain of the final austenite fraction (10%) is more compressive (or less tensile) than the initial 20%. Also if it is an elastic strain effect then there has to be a balancing albeit smaller change in the martensitic lattice parameters. Although harder to measure, since the strain in the majority phase is smaller and the tetragonal martensite is more difficult to refine (with an  $a_0$  and a  $c_0$ ), preliminary evidence suggests that the martensitic lattice parameters do indeed move in the opposite direction. However the Rietveld analysis indicated that more than one martensitic phase may be present and thus the complementary martensitic result needs further analysis. Consequently it is premature to say that the change in the austenite lattice parameter is really due to elastic strain. (The magnitude seems large and the sign of the stress change is counterintuitive although possible). Another explanation for the difference seen in figure 4, (which is undoubtedly real) might be that the average composition of the final austenite differs from the initial fraction (which might happen if the carbon were irregularly distributed). Computational modeling and further experiments are being performed to pursue this. However the potential of this approach is the possibility to measure elastic strain incompatibility thereby indirectly quantifying the effect of TRIP.

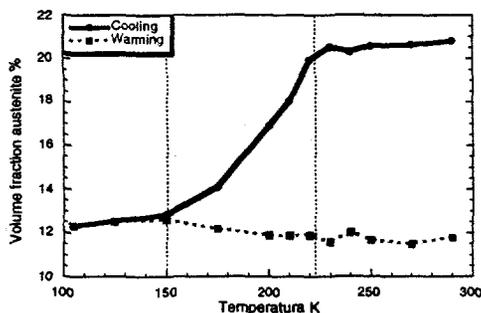


Fig. 3 Volume fraction of retained austenite in a quenched 5180 steel cylinder during cooling from ambient to 100K and during reheating.

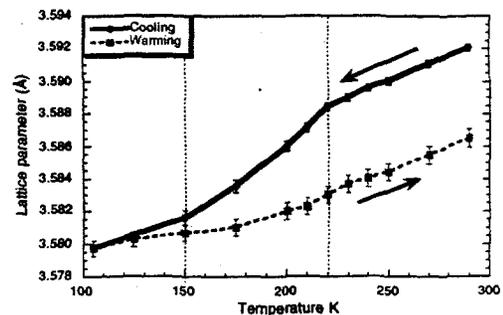


Fig 4. Changing lattice parameter in the diminishing austenite phase fraction throughout cooling to 100K and subsequent warming to ambient.

## 5 REAL TIME TRANSFORMATIONS AT 670°C IN STAINLESS STEEL

In both of the preceding examples, the transformations were controllable and could be halted by relieving the external stimuli. However, in many cases, transformation kinetics themselves are of interest, and the inherent time required for collection of diffraction data becomes the limiting feature. One example concerns deformed 304 stainless steel in which, at elevated temperatures, strain induced martensite reverts to austenite. The retransformation kinetics are of relevance because the rapidity at which the reversion occurs impacts corrosion sensitivity. However at 670°C the retransformation is largely complete in less than hour. This precludes measurements using conventional neutron diffractometers which typically require times in excess of 30 minutes to record an individual diffraction spectrum. Consequently a faster technique is needed.

Fortunately at a pulsed source it is possible to use Bragg edge diffraction in which, instead of examining the scattered radiation, one examines "edges" that form in the transmitted spectrum. Edge patterns may be thought of as inverse diffraction patterns (although not with sharp peaks), since they are formed as a result of diffracted neutrons scattered out of the incident spectrum. Moreover since neutrons scattered into  $4\pi$  steradians contribute to each edge they are defined much faster than a conventional peak in a detector subtending a, generally, small solid angle. Thus, edge diffraction spectra can be determined in timescales much shorter than can conventional scattered spectra (albeit with poorer signal to noise characteristics).

In the experiment on the deformed stainless steel, coupons, of initially  $\approx 80$  vol% martensitic composition, were placed in a furnace at 670°C to initiate retransformation[3]. A selection of sequentially recorded edges are shown for a short section of the spectrum for the austenitic [220] edge in Figure 5. 172 seconds after the coupon was placed in the furnace the edge is poorly defined but becomes progressively sharper with increasing time. Each individual spectrum took 60 seconds to record. Changing phase fractions were quantified by recording the increasing or, in the case of the martensite, decreasing edge heights. Respective phase fractions are shown with time resolution of about 1 minute in Figure 6. This data provides direct *in situ* crystallographic measurement of bulk transformation kinetics, a result that would be impossible to obtain using XRD or dilatometry (the two conventional alternatives).

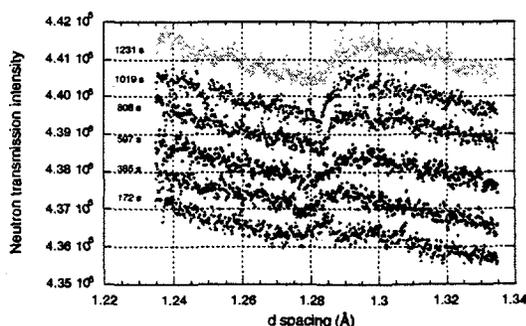


Fig 5. A temporal series of austenitic [220] Bragg edge showing its increasing definition for increasing time after the specimen was placed in the furnace.

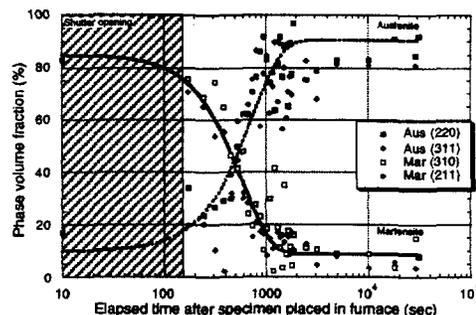


Fig 6. Transformation kinetics are obtained by fitting to all fitted edges. The fits were constrained to agree with the independently measured end composition.

## 6. GENERAL COMMENTS

Neutrons are under-exploited for studying phase transformations in engineering materials. Relating bulk texture to transformations in shape-memory alloys has the potential to significantly improve our understanding of these materials. If the TRIP effect proves to be quantifiable, then progress could be made in validating the constitutive models used in prediction of distortion and residual stress resulting from carburizing. Finally the use of Bragg edge diffraction to record real time transformation kinetics ultimately holds the possibility for simultaneous and rapid phase, temperature (by resonance radiography) and strain measurements in bulk specimens.

## 7. ACKNOWLEDGMENTS

Data for the cryogenic experiment described in 4. were obtained using the HRPD at ISIS and preliminary data were recorded at IPNS a user facility operated by the US DOE under contract W-31-109ENG-38. We acknowledge Julio Maldonado and Raj Vaidyanathan for preparing the 304 stainless and NiTi specimens respectively, and Dallas Masters for performing much of

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## 8. REFERENCES

- D.C. Dunand et al "NiTi and NiTiTiC composites Part IV: Neutron diffraction study of compressive deformation and shape memory recovery, *Met Trans* Vol 27A In press (1996)
- F.D. Fischer, "A micromechanical model for transformation plasticity in steels" *Acta Met.* Vol 38. No 8 , pp1535-1546, 1990
- K. Meggers et al. "Real time neutron transmission investigation of the austenite bainite transformation in gray iron"; *Nuclear Instruments and methods in Physics research B* 88 pp423-429, 1994.
- M.A.M. Bourke et al. "Real time measurement by Bragg edge diffraction of the reverse ( $\alpha' \rightarrow \gamma$ ) transformation in a deformed 304 stainless steel" *Journal of Materials Science and engineering*; In press 1996.



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