

IMPERIAL COLLEGE LONDON

Diffraction Investigations of High Temperature Shape Memory Alloys

by

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A thesis submitted in partial fulfillment for the
degree of Doctor of Philosophy

in the

Faculty of Engineering
Department of Materials

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Abstract

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Shape memory alloys are intermetallic materials with a unique ability to revert to a predefined physical shape by virtue of diffusionless transformations. Recent interest by aerospace and automotive industries to exploit the functionalities of these materials in future energy efficient designs has renewed scientific research in this field. However, the current understanding of transformation hysteresis is inhibited by experimental difficulties associated with viewing the transformations and therefore most of our knowledge is confined to symptomatic bulk properties such as those accessible from calorimetry and dilatometry.

In the current study, in situ synchrotron X-ray diffraction (SXRD) was used to accurately document the adaptability of unit cells of participating phases during transformation in a series of high temperature shape memory alloys (HTSMAs). Selected alloys based on NiTi, ZrCu and NiMnGa systems were prepared in vacuum arc melter, homogenized and rolled to grain size adequate for SXRD experiments. The resulting diffraction patterns were Rietveld refined and the evolution of unit cell parameters of participating phases were recorded as a function of temperature.

It was observed that the lattices of participating phases undergo a significant overall dilation during transformation. The lower symmetry martensite unit cell was observed to undergo unprecedented anisotropic strains, reaching as high as 1.2% in certain alloys. The high temperature higher symmetry austenite was observed to complement the changes in martensite lattice during heating and vice versa was observed during cooling. These changes were mostly observed in final stages of transformation. Surprisingly, a negative coefficient of thermal expansion was observed in the b lattice parameter of the monoclinic martensite in NiTi based alloys. The implications of such strains on the current phenomenological martensitic transformation models that takes into consideration lattice parameters away from the transformation regime for prediction of orientation between participating phases has been discussed.

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Abbreviations

bcc	body centered cubic
BF	Bright Field
COP	Coefficient Of Performance
DECs	Diffraction Elastic Constants
DF	Dark Field
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EBSD	Electron Back Scatter Diffraction
ED	Extrusion Direction
EDM	Electro Discharge Machining
EDX	Energy Dispersive X-ray spectroscopy
EPMA	Electron Probe Micro Analyzer
EPSC	Elasto Plastic Self Consistent
ESRF	European Synchrotron Radiation Facility
ETMT	Electro Thermo Mechanical Testing
fcc	face centered cubic
fSMA	ferromagnetic Shape Memory Alloy
GSAS	Generalized Structure Analysis System
HEM	Homogenous Effective Medium
HTSMA	High Temperature Shape Memory Alloy
HPV	Habit Plane Variant
HTSMAs	High Temperature Shape Memory Alloys
LaB₆	Lanthanum hexa Boride
LTSMA	Low Temperature Shape Memory Alloys

MFIS	M agnetic F ield I nduced S trains
MEMS	M icro E lectro M echanical S ystems
ND	N ormal D irection
ORs	O rientation R elationships
OWSME	O ne W ay S hape M emory E ffect
PTMT	P henomenological T heory of M artensitic T ransformation
SMA	S hape M emory A lloy
SMA s	S hape M emory A lloys
SEM	S cannning E lectron M icroscope
SFE	S tacking F ault E nergy
SME	S hape M emory E ffect
sXRD	synchrotron X -ray D iffraction
TD	T ransverse D irection
TEM	T ransmission E lectron M icroscopy
TT	T ransformation T emperature
TT s	T ransformation T emperatures
TWSME	T wo W ay S hape M emory E ffect
VAM	V acuum A rc M elting
XRD	X -ray D iffraction

Symbols

2θ	$2\times$ diffraction angle	$^\circ$
$a_{B19'}$	‘a’ lattice parameter of B19’ martensite unit cell	$\text{\AA}$
a_{B2}	‘a’ lattice parameter of B2 austenite unit cell	$\text{\AA}$
a_t	‘a’ lattice parameter of tetragonal martensite unit cell	$\text{\AA}$
A_f	Austenite finish temperature	$^\circ\text{C}$
A_p	Austenite peak temperature	$^\circ\text{C}$
α_{th}	Coefficient of thermal expansion	$^\circ\text{C}^{-1}$
A_s	Austenite start temperature	$^\circ\text{C}$
$b_{B19'}$	‘b’ lattice parameter of B19’ unit cell	$\text{\AA}$
β	Monoclinic unit cell angle in setting 2	$^\circ$
c	calculated	—
C_{11}	Elastic constant	GPa
C_{12}	Elastic constant	GPa
C_{44}	Elastic constant, represents resistance to shear on (110), along [100]	GPa
C'	Subtractive linear combination of elastic constant	GPa
$c_{B19'}$	‘c’ lattice parameter of B19’ unit cell	$\text{\AA}$
c_t	‘c’ lattice parameter of tetragonal martensite unit cell	$\text{\AA}$
D	Interplanar spacing	$\text{\AA}$
Δ	Maximum lattice change during transformation	$\text{\AA}$
$\dot{\epsilon}$	Strain rate	s^{-1}
$\dot{\epsilon}^c$	Strain rate in a single	s^{-1}
e	experimental	—
e_{elr}	Elastic strain recovery	—
e/a	Electron to atom ratio	—

η_1	Twinning direction	—
η_2	Reciprocal twinning direction	—
f_0	fraction of parent grain	—
Γ	Accumulated shear strain	—
γ	Monoclinic unit cell angle in setting 1	°
h	Time in hours	h
K	Additive linear combination of elastic constant	GPa
K_1	(normal to) primary twinning plane	—
K_2	(normal to) reciprocal twinning plane	—
M_f	Martensite finish temperature	°C
M_s	Martensite start temperature	°C
M_p	Martensite peak temperature	°C
Ψ	Azimuthal angle across the diffraction ring	°
s	Twinning shear	—
σ_{appl}	Applied stress	MPa
$\dot{\sigma}$	Stress rate	MPas ⁻¹
$\dot{\sigma}^c$	Stress rate in a single grain	MPas ⁻¹
T	Temperature	°C
T_c	Curie temperature	°C
τ^s	Critical resolve Schmid stress	MPa or GPa
$V_{B19'}$	B19' unit cell volume	Å ³
V_{B2}	B2 unit cell volume	Å ³
V_P	Parent twin volume fraction	—
V_C	Child twin volume fraction	—

Dedicated to my parents, my wife and my siblings. . .

Chapter 1

Introduction

Shape Memory Alloys (SMAs) are intermetallic materials that have ability to remember a high or a low temperature shape. The Shape Memory Functionality (SMF) in such materials is fundamentally based on co-ordinated diffusionless displacement of atoms eventually leading to a solid-solid phase change, a phenomenon that is referred to as martensitic transformation in steel metallurgy [Bhadeshia and Honeycombe, 2006]. These transformations can be stress and/or temperature induced, as schematically shown in Figure 1.1. As in steels, the higher temperature, high symmetry phase is referred to as Austenite and the lower temperature low symmetry phase as Martensite. However, unlike in steels, in SMAs non-equilibrium cooling is not an essential condition for the temperature induced formation of martensite from austenite. While the martensite formed in steels is metastable, in SMAs, it is a perfectly stable below a critical temperature that is characteristic to the alloy system and composition.

At the core of these diffusionless phase transformations is a inhomogenous twinning assisted lattice deformation which is proved to be energetically more favourable than the homogeneous dilatation [Lieberman et al., 1955]. The crystallographic aspects of twinning are explained in detail in the literature review, but essentially, twins are undulations/defects in an otherwise perfect lattice that are related to the matrix phase by a reflection about a specific plane (habit plane) and a rotation about a specific axis. SMAs are a special case where the complete transformation proceeds *via* twinning. The resulting microstructure is a network of self accommodating twins as shown in Figure 1.2

The two way shape memory effect (TWSME) is a specific case where selected alloys in certain microstructural states tend to remember both high and low temperature shape. It is generally induced in alloys after a few thermal cycles that are widely referred to as ‘alloy training’ in the literature [Meng et al., 2000]. A true mechanistic understanding for this behaviour is not yet

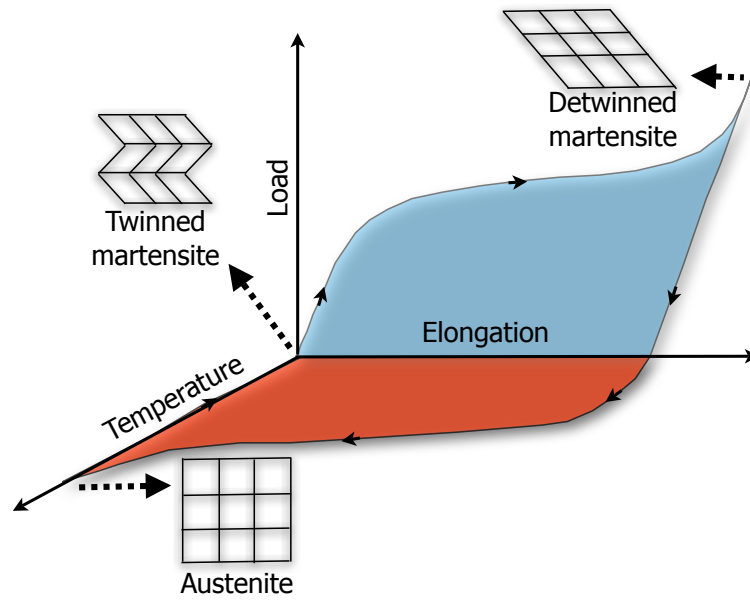


FIGURE 1.1: Illustration of thermoelastic effect in shape memory alloys

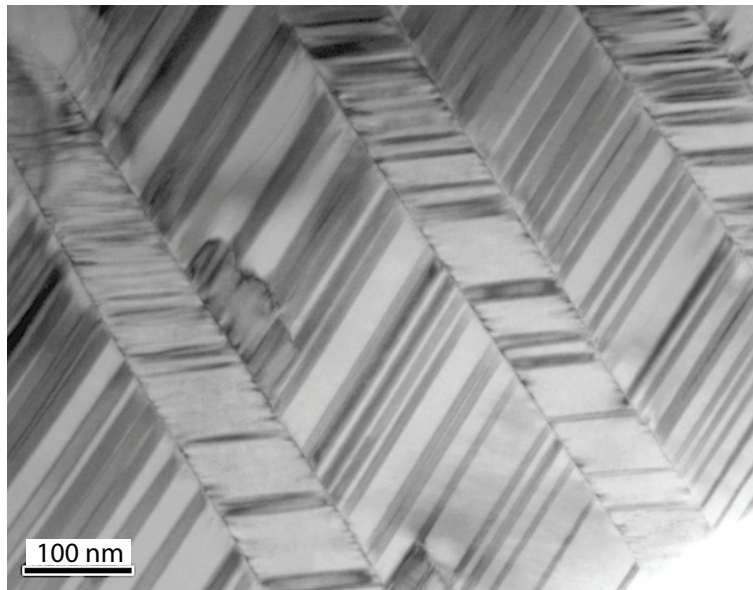


FIGURE 1.2: Self-accommodating twins in $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$, imaged using BF TEM (see results chapters).

known, but it is widely believed to be due to residual stresses arising from dislocations [Otsuka et al., 1999](page 44).

It is also possible for the material to be placed into a one way shape memory (superelastic) condition, where the low temperature martensitic configuration is not fixed. In this configuration, the austenite grains are imagined to remain constant after each heating cycle, but variant selection can occur differently depending on the loading history within each austenite grain

during each cooling interval. Therefore the high temperature shape is fixed (remembered) but the low temperature shape is not.

A third actuation option is to load material in the superelastic condition. In fact two types of these scenarios can be imagined. In the first, the material is in the austenite phase at the operating temperature, but barely. Application of a load then causes the material to transform to the martensite, giving rise to a plateau in the stress-strain curve. In the second, the material is already in the martensite phase, but on application of a critical stress the martensite detwins, also giving rise to a plateau in the stress-strain curve. In certain cases, rather than observing a plateau on loading, transformation can be progressive with load, giving rise to an apparent softening during the elastic portion of the stress-strain curve; there is a continuum between elastic-plastic behaviour and completely superelastic behaviour with a load plateau.

While NiTi-based superelastic / shape memory alloys have been known for many years, especially in the well-known arterial stent application, instances of their use in engineering structures are rather limited. The case of the arterial stent is instructive. Here, the alloy manufactured stent is first cooled by placing it onto a water-cooled insertion tube, at which point it shrinks for insertion into the body. Once the stent has been placed in the desired location, it is then allowed to warm up to body temperature and transforms to the austenite. At this point it holds the artery open and remains in the austenite condition throughout its service life.

In contrast, actuator applications have a different set of demands. In these applications, actuation is achieved by cycling the NiTi between the austenitic and martensitic states, so rather than one cycle, thousands of transformation cycles are required. The well-publicised prototype Rolls-Royce bypass duct actuator [Birch and Webster, 2006] uses a one way thermal shape memory alloy with the low temperature shape controlled by the application of a bias load by a retaining Ti alloy strip. The device is then heated to achieve actuation in a low weight structure that also has a capability to carry a reasonable mechanical aeroelastic load. This device then has a low part count and requires minimal or no maintenance. Such structures are limited by the range of transformation temperatures available from shape memory alloy materials, and by any material evolution that occurs through cycling. The present thesis is concerned with the former problem - raising the maximum transformation temperature. Two RAs, Drs. Seema Raghunathan and Nicholas Jones, had parallel projects on the material evolution during cycling.

The ‘more electric aircraft’ and ‘more electric engine’ concepts provide part of the motivation for the present work. In these concepts, hydraulic actuation and heating/cooling of aircraft components is replaced by electrically-powered systems, removing the need for separate hydraulic and bleed-air systems distributed throughout an aircraft. This would then result in an increase in modularity, a reduction in system complexity and a corresponding reduction in development

times and technical risk. It is also thought that this might increase robustness of the airframe system and allow for breakthrough reductions in weight.

Aero gas turbines use fuel cooling and bleed air extensively to manage the thermal loads on different parts of the engine, and given the size of these loads then mitigating these is likely unfeasible, and in any case, pre-heating the fuel is a good thing up to a point. However, there are many opportunities where actuation of control surfaces might allow for improved optimisation of the engine across all points of the flight cycle, and due to the weight of mechanical actuators, only relatively few of these opportunities are usually exploited. Therefore there exist many opportunities for shape memory actuators, if the alloys could operate at the temperatures required.

SMA's with transformation temperatures higher than 125 °C are classified as high temperature shape memory alloys (HTSMA's) [Van Humbeeck, 1999a]. Given that even the bypass air in an aero gas turbine may have an exit temperature in excess of 80 °C, while the gas stream temperature on entry to the turbine is in excess of 1600 °C, then the development of high temperature shape memory actuator materials is naturally of technological interest.

In this thesis, a number of possible shape memory alloy systems are explored that might provide a basis for the development of inexpensive HTSMA actuators. The starting point is NiTi, but ZrCu and NiMnGa based systems are also explored. Some of the ZrCu based HTSMA's have been reported to be non-thermoelastic [Van Humbeeck, 1999a] while NiMnGa Heusler alloys are magnetic but very brittle in their polycrystalline form. NiTi based alloys with Pt, Pd and Au have very high transformation temperatures but the cost of making these alloys restricts their prospects as potential candidates in structural applications, except perhaps in space applications. NiTi based alloys with Zr and/or Hf have attracted much attention due to their low cost, ease and practicality of being used as structural alloys.

The focus of the project was the preparation of hot-worked polycrystalline alloys that could then be characterised *in situ* through the transformation cycle using synchrotron X-ray diffraction. While initially investigating the transformation behaviour based on whole-ring Rietveld refinement of volume fractions for correlation with DSC, it was found that the lattice parameters appeared to deviate significantly through the transformation process, and this became a major focus of the work. The main results of this investigation form the first experimental chapter.

Initially, an aim of the project was to develop a micromechanical model of the transformation behaviour in collaboration with an RA, but this proved to be prohibitively costly in manpower. However, as an initial exploration of the feasibility of examining this aspect, a self-consistent model was fitted to some existing data for near- α brasses, and this forms Appendix A.

Some TEM images are also provided in this thesis, as one possibility was to examine the twin variant and orientation relationships in light of the lattice parameters obtained from the synchrotron radiation experiments using the phenomenological theory of martensite transformations. However, while dark field (DF) imaging and classification of the twin types did prove to be possible, completion of this aspect of the work did not prove to be possible in the time available.

At the start of the project, we examined a NiTi shape memory alloy wire, which was published as a small letter paper in [2008](#). The majority of that work was performed by Dr Raghunathan, but it is also provided for the reader's interest as Appendix B.

The main experimental chapters are then explored by alloy - first the Ni(Ti,Hf,Zr) and (Ni,Cu)(Ti,Hf,Zr) alloys, then a $\text{Zr}_2\text{Cu}(\text{Co},\text{Ni})$ alloy and then finally an off-stoichiometric N_2MnGa alloy. Some Conclusions and suggestions for Further Work are then provided.

Chapter 2

Literature review

Shape Memory Effect (SME) was first observed in equiatomic AuCd alloy [Olander, 1932] and later in 1963 Buehler et al. reported this unique effect in equiatomic NiTi. Shape Memory Alloys (SMAs) operate by a martensitic, long-range diffusionless transformation from one crystal structure to another; as explained in Chapter 1, the transformation may be superelastic or it may be temperature induced. In the former case, they are of utility as low modulus, high strain springs and in the latter as thermal actuators.

The initial investigations on this class of functional materials were focussed at addressing a vast number of complex issues associated with functional stability and crystallography. Undoubtedly, NiTi and its ternary and quaternary alloys emerge to be the most investigated in this process. This exclusivity towards NiTi based alloys was primarily driven by a relatively stable SME, large dilatational strains and partly by the systems strong biocompatibility [Kujala et al., 2004; Berger-Gorbet et al., 1996]. Earlier investigation were directed towards learning the crystallography of austenite, martensite and other precipitates/phases like TiNi_3 [Taylor and Floyd, 1950], Ti_2Ni [Mueller and Knott, 1963], Ti_3Ni_4 [Tadaki et al., 1986; Khalil-Allafi et al., 2002], Ti_2Ni_3 [Hara et al., 1997]. These precipitates are known to alter the transformation behaviour considerably by both altering the alloy matrix composition [Funakubo, 1987] and by imposing coherency constraints [Ishida et al., 1997; Zhang et al., 2003] on the transforming lattices. Some of these phases appear as line compounds in the vicinity of equiatomic composition in the binary NiTi phase diagram, Figure 2.1.

Regular near-equiatomic NiTi has transformation temperatures (TTs) in the range of 0 to 20 °C for the on-cooling transformation and 30 – 80°C for the on-heating transformation, by Liu et al. [1997]. The existence of a hysteresis in the TTs is commonly attributed to the energy dissipated in moving the austenite/martensite interfaces [Zarnetta et al., 2007; Delville

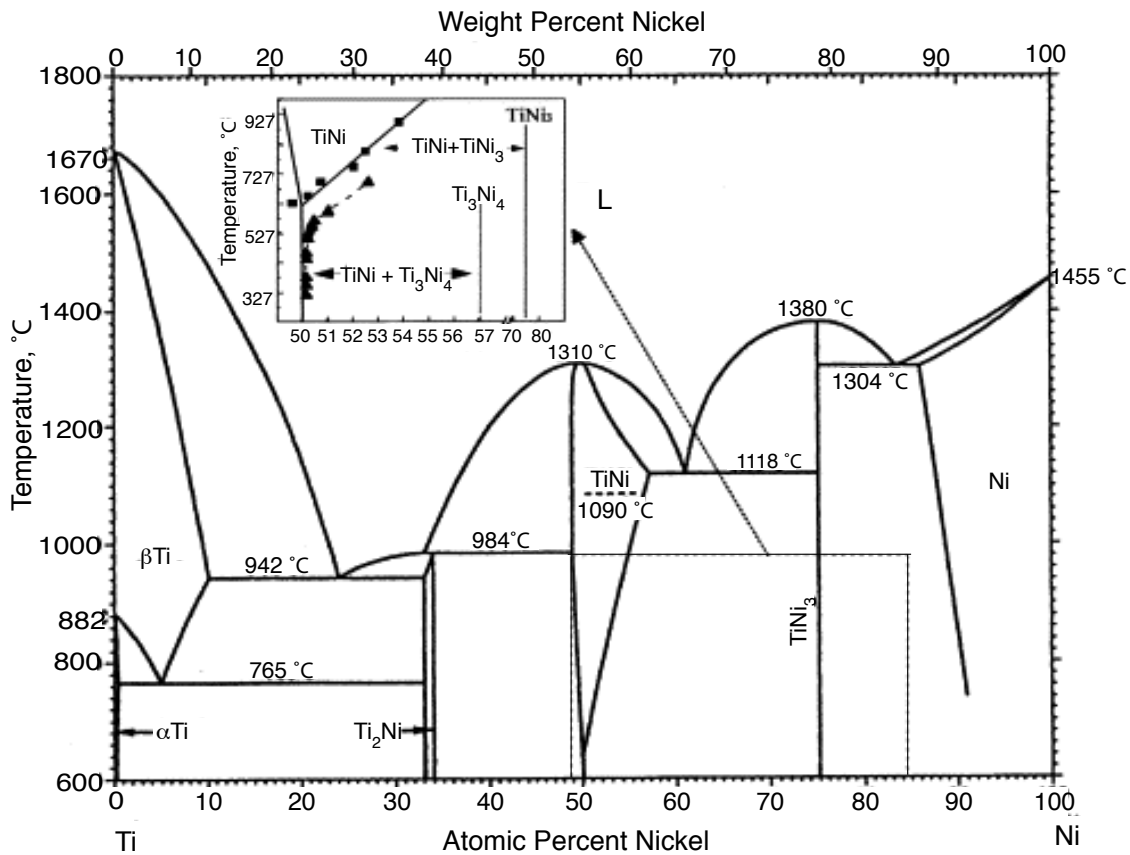


FIGURE 2.1: Binary Nickel Titanium equilibrium diagram, after [Massalski et al. \[1990\]](#)

[et al., 2010](#); [Zarnetta et al., 2010](#)] which is in turn related to the availability of variants, self accommodation [[Madangopal, 1997](#)] and the interface strains that require the generation of interface defects [[Pond et al., 2003](#)]. Indeed, when the interface strain is minimised according to the phenomenological theory of martensite transformation (PTMT), the hysteresis is also minimised [[Cui et al., 2006](#)].

A major problem for the widespread deployment of practical SMA actuator is functional stability; frequently it is observed that the transformation temperatures and strain evolve on repeated, thermal [[Wagner et al., 2010](#)], thermomechanical [[Eggeler et al., 2004](#); [Ma et al., 2010](#)] or even just thermal cycling under a constant load [[Jones and Dye, 2011](#)]. It is essential that the properties of a given SMA does not deviate considerably with cycling within the rated temperature-pressure regime. The prospect is raised of either an impaired fatigue response or of the on-cooling transformation dropping below the ambient temperature of the device environment, and hence cessation of function. It is usually felt that this evolution is due to build up of defects, such as dislocations produced at the martensite-austenite interface [[Hamilton et al., 2004](#)]. In Cu based SMAs dislocations have even been observed to serve as heterogeneous martensite nucleation sites [[Ibarra et al., 2007](#)]. Further to this, [Simon et al. \[2010\]](#) observed

multiplication of dislocations in NiTi single crystals during thermal cycling. These studies emphasise the importance of defects in shape memory alloys. Therefore much research has focussed on mechanical processing to provide a stable defect population, *e.g.* by the production of a very fine grain size and/or by the introduction of additional stable intermetallics such as, TiNi₃ [Taylor and Floyd, 1950], Ti₂Ni [Mueller and Knott, 1963] and Ti₃Ni₄ [Tadaki et al., 1986; Khalil-Allafi et al., 2002], although a clear mechanistic understanding of the role of defects and their evolution during transformation is still elusive.

The versatility of applications of any given metallic alloy strongly depends on its corrosion resistance. In biological environments, the corrosion resistance of NiTi alloys is observed to be comparable to the most commonly used Ti6Al4V [Rondelli, 1996] alloy, which is also a conventional choice in aerospace industry for sub 300 °C applications [Peters et al., 2003]. For bio applications, a further limitation applies on the alloying elements used and their purity owing to chances of cytotoxicity [Wever et al., 1997]. NiTi has been successfully used in various biomedical applications, for example, vena caval or arterial stents [Duerig et al., 1999], teeth [Andreasen, 1980] and bone reinforcements etc, however, the passivity of any non-standard NiTi based alloy should be carefully evaluated to avoid cytotoxicity arising from Ni dissolution. Unlike in biomedical applications, alloy purity may not be pursued as critically in automotive and aerospace industries as long as the rate of degradation of shape memory functionality remains within a certain design limit. Ultimately, the purity of alloying elements needs to be weighted against the cost benefits and the alloys functional reliability. It is a well known fact that Carbon and Oxygen are the two most commonly observed impurities in both ingot and powder metallurgy routes of alloy production. Oxygen in NiTi is reported to have indirect effect on SME, it is observed to react with Ti rendering the matrix Ni rich resulting in reduction of TTs [Funakubo, 1987], further details are provided in Section 2.4.

SMAs are used or suggested for a wide variety of applications [Hartl and Lagoudas, 2007; Chau et al., 2006; Van Humbeeck, 1999b] that each exploit different features of the behaviour. Austenitic seismic dampers [Dolce and Cardone, 2001] use transformation in each load cycle, making use of the large recoverable strain and hysteresis. In contrast, martensitic shape memory materials detwin the martensite at low temperatures and then recover the shape on heating; this is the phenomenon used in arterial stents [Duerig et al., 1999]. NiTi wires have been posited to actuate bistable air flow structures such as doors and air inlets in aircraft using thermal actuation. Recently, bimetallic NiTi / Ti thermal actuators have been suggested for noise control in gas turbine variable area nozzles [Birch and Webster, 2006; Calkins et al., 2006; Hartl and Lagoudas, 2007]. This leads to the suggestion that high temperature shape memory alloys (HTSMAs) could be used for airflow control elsewhere in gas turbines [Webster, 2006]. However,

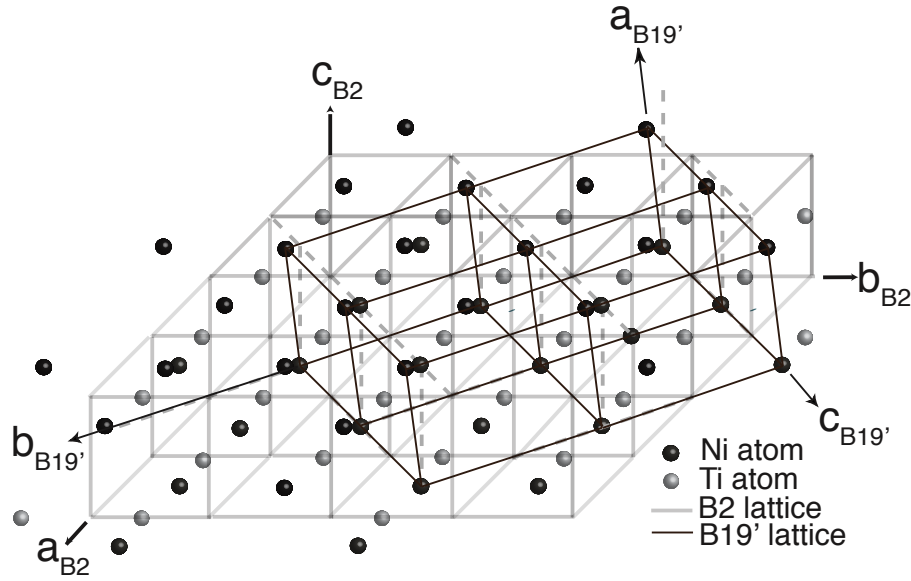


FIGURE 2.2: Illustration of B2 and B19' orientation relationship in equiatomic NiTi.

having a detailed understanding of the micromechanics of the transformations becomes more critical as multi-cycle, structural and more safety-critical components are suggested.

The primary objective of this review is to gather a broad perspective of SME in HTSMAs based on the most practical NiTi and ZrCu systems and out of sheer curiosity in ferromagnetic HTSMAs based on NiMn. It is not an attempt to present a full review of these alloy systems but it is a survey addressed in light of classic avenues like the phenomenological theory of martensitic transformation (PTMT) [Lieberman et al., 1955] and the concept of elastic softening and/or lattice collapse along certain crystallographic directions in body centered cubic (bcc) lattices as originally proposed by Zener in 1948. Further in this chapter, a review of the twinning assisted inhomogeneous dilation which forms the crux of martensitic transformation and the crystallographic aspects of twinning are covered in the two subsequent sections followed by a short review of each of the three alloy systems mentioned earlier with emphasis on NiTi based HTSMAs. Finally, a comprehensive review on recent developments in EPSC modelling which could be potentially used in tandem with the PTMT to predict the lattice strains and far field macroscopic response of SMAs is presented in Appendix A.

2.1 Stability of austenite and the need for twinning

In a cubic lattice, the elastic coefficients C_{44} , C_{11} and C_{12} may be interpreted, either individually or as additive or subtractive linear combinations like $K \equiv (C_{11} + 2C_{12})/3$ and $C' \equiv (C_{11} - C_{12})/2$ respectively, as a measure of resistance of lattice to elastic distortion. C_{44} represents resistance

to shear on (100) plane in [010] direction and K and C' are resistances to deformation in presence of a hydrostatic pressure and to shear along (110) plane in $[1\bar{1}0]$ direction respectively. It should be noted that for cubic crystals C_{44} also represents resistance of lattice to $\{001\}[110]$ shear [Otsuka and Ren, 2005](page 573). Zener [1948] coined the idea that a bcc hard ball lattice is the most unstable of all the three cubic Bravais lattices based on the logic that the central atom in a bcc unit cell is a pivot for the atoms on the diagonally opposite corners of the cube and therefore there would no resistance to a coordinated movement of atoms on a (110) plane along $[1\bar{1}0]$ direction, *i.e.*, in a hard ball bcc lattice C' could approach zero under exceptional circumstances.

It is logical for a given alloy system to minimize its energy during a diffusionless transformation by opting for orientation relationships (ORs) that reduce the coherency strains between the participating phases. For example, the primary OR in a $B2 \rightarrow B19'$ transformation in near equiatomic NiTi is $\{110\}_{B2} \parallel (010)_{B19'}$ [Raghunathan et al., 2008], illustrated in Figure 2.2. It is observed to be the most probable in terms of difference in areas of intersecting crystallographic planes of B2 and B19'. The transformation of a single crystal austenite to martensite can either proceed by a uniform change in dimensions of participating lattice (homogeneous constriction/dilation) or non uniformly by self induced lattice defects like twins (inhomogeneous dilation), both these modes are schematically depicted in Figure 2.3 and the latter is observed to be more energetically favourable [Lieberman et al., 1955]. It is apparent based on the Zener's hard ball descriptive model that the inhomogeneous twinning assisted deformation in a bcc/B2 lattice is most likely to seed on a $\{110\}$ plane through a shear along $\langle 110 \rangle$ direction, referred to as primary shear hereafter. Ren et al. [2001] through ultrasonic measurements showed that such shear is facilitated by the softening of C' in the B2 lattice. They also reported considerable softening prior to transformation in the C_{44} of austenite which dictates the $\{001\}[110]$ shear which is essential for the monoclinic angular deflection.

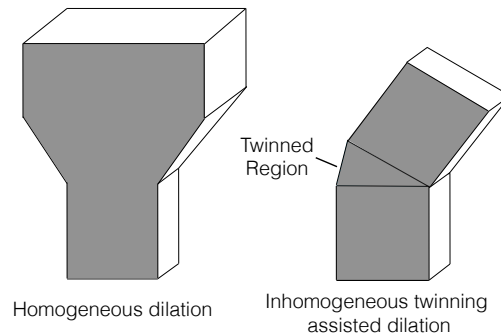


FIGURE 2.3: Homogeneous and inhomogeneous dilation

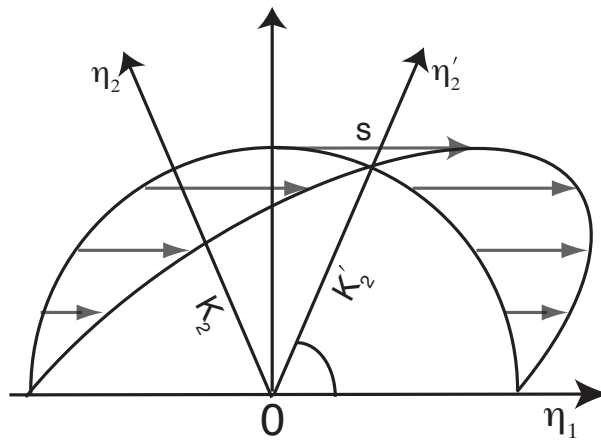


FIGURE 2.4: Geometric illustration of twinning

2.2 Crystallographic aspects of twinning

As per the classical theory of twinning [Bilby and Crocker, 1965; Jaswon and Dove, 1960], a twin is identified by five elements, videlicet, the twin plane (K_1), reciprocal twin plane (K_2), twinning direction (η_1), reciprocal twinning direction (η_2) and the twinning shear (s). Based on these, twins can be divided into three categories

- type I: where K_1 and η_2 are rational indices and the two twin crystals are related by a mirror symmetry with respect to K_1 .
- type II: where two lattice vectors lie on K_2 plane and the third lattice vectors is parallel to η_1 direction. While K_2 and η_1 are represented by rational indices, the other two elements are irrational and the twinned crystals are related by a π radian rotation about the η_1 axis.
- compound twins: a case where all four elements, K_1 , K_2 , η_1 and η_2 are rational and the twin crystal have both symmetries, *i.e.*, mirror symmetry of type I and rotation symmetry of type II.

2.3 Shape Memory Alloy systems

Following AuCd, SME was reported in various alloy systems, a near to complete list of these alloys is provided in Table 2.1 along with their respective transformation and hysteresis temperatures. Most of these alloy systems involve an ordered diffusionless change from a high temperature high symmetry austenite phase to a low temperature low symmetry martensite

TABLE 2.1: Some of the commonly known shape memory alloy systems and their properties, taken from Funakubo [1987] are presented in this table. Information for alloys systems marked *, **, †, ++, ‡, ‡‡ and $\diamond$ are adopted from AbuJdom et al. [1992], Huisman-Kleinherenbrnik [1991]; Van Humbeeck [1999a], Grossmann et al. [2009], Cacciamani et al. [2006], Firstov et al. [1997], Yang and Mikkola [1992] and Lanska et al. [2004] respectively.

Alloy	Type of Transformation	M_s , °C	Transformation Temperature Hysteresis, °C	Ordered or Disordered
AgCd	B2→M2H	-190 to -50	15	Ordered
AuCd	B2→M2H	30 to 100	15	Ordered
CuAlNi	DO ₃ →2H	-140 to 100	35	Ordered
CuAuZn	L21→M18R	-190 to 40	6	Ordered
CuSn	DO ₃ →2H	-120 to 30		Ordered
CuZn	B2→9R or M9R	-180 to -10	10	Ordered
CuZnX	B2→9R or M9R	-180 to 100	10	Ordered
X = Si, Sn, Al, Ga				
InTl	FCC→FCT	60 to 100	4	Disordered
NiAl	B2→M3R	-180 to 100	10	Ordered
FePt	L1 ₂ →ordered BCT	~ -130	4	Ordered
FePd	FCC→FCT→BCT	~ -100		Disordered
MnCu	FCC→FCT	-250 to 180	25	Disordered
NiTi	B2→B19 or B19'	-50 to 100	20	Ordered
Ni(Ti-X)* (X = Hf, Zr, Hf+Zr)	B2→B19'	80 to 320	—	Ordered
(Ni-X)Ti** (X = Pt, Pd, Au, Rh)	B2→B19	0 to 1000	—	Ordered
(Ni-X)Ti† (X = Cu)	B2→B19', Cu<9 at% B2→B19→B19', Cu>9 at%	0 to 120	~ 15 ~ 7	Ordered Ordered
(Ni-X)Ti++ (X =Fe < 3 at.%)	B2→R→B19'		B2→R=~ 3 R→R19' = 30 - 40	Ordered Ordered
Zr ₅₀ Cu ₂₅ Co _{50-x} Ni _x ‡ (x = 0 to 25)	B2→B19' and Cm	0 to 750	~ 200 °C	Ordered
Ni(Mn-X)‡‡ (X = 0 to 7 at.%) Cr, Ti, Si Al, Nb, V Co Mo, Fe Mg and Sn)	B2/L2 ₁ →Tetragonal or orthorhombic	550 to 750	-	Ordered
Ni ₄₇₋₅₅ Mn ₂₄₋₃₃ Ga ₂₀₋₂₂ ◊	B2→Tetragonal/ Orthorhombic/ Monoclinic	30 to 257	~ 5 to 25	Ordered

either in single or multiple steps. The alloys with A_f below ≈ 120 °C are generally classified as low temperature shape memory alloys (LTSMAs) [Van Humbeeck, 1999a]. Each of the ternary higher order alloy in Table 2.1 is based on an intermetallic line compound (referred to as ‘base alloy’ here afterwards) in a certain binary alloy system. In most instances, the base alloy has a near equiatomic composition and higher order alloys can be prepared by stoichiometrically replacing one of the primary alloying elements. For example, for a Ni(Ti-Hf) ternary HTSMA NiTi is the base alloy and addition of Hf to replace Ti is observed to increase the TTs considerably. Therefore, a further classification of the higher order alloys is possible by taking into consideration the amount of stoichiometric alloying plausible without any significant precipitation of Ni or Ti rich phases, this limit is ≈ 20 at.% Hf in case of Ni(Ti-Hf). It is evident from these studies that potential alloys operational over a temperature range of interest can be designed by either altering the stoichiometry or by replacing one of the primary alloying elements by a ternary or a quaternary element. Majority of base alloys are brittle due to their inherent intermetallic nature [Van Humbeeck, 1999a] but in certain select systems, stoichiometric addition of third and fourth element is observed to improve the ductility considerably. For example, enhanced ductility has been reported Firstov et al. [1997] in SMAs formed by stoichiometric addition of Ni as a replacement for Co in $Zr_{50}Cu_{25}Co_{25}$.

The TTs of alloys listed in Table 2.1 are generally sensitive to deviations in composition away from a specific stoichiometry, for the case of NiTi based alloys this will be discussed in detail in the next section. The crystal structure of austenite in all NiTi based alloys is reported to be B2 while martensite is observed to assume B19 (orthorhombic), B19' (monoclinic) or R (trigonal) crystal structure depending on the alloying and the thermo mechanical history. In certain alloys and microstructural states, the R and B19 phase could also be an intermediate phases in the final formation of B19'. Very high TTs (> 500 °C) are only available by excessive stoichiometric alloying of a select few alloy systems like (Ni-X)Ti; X = Pd, Pt and Au [Huisman-Kleinherenbrink, 1991], the $Zr_{50}Cu_{25}Co_{50-x}Ni_x$ alloys with Ni atom fraction x in the range of 15-25 at.% [Firstov et al., 1997] and the Ni-Mn based ternary alloys. Due to high cost of production, the (Ni-X)Ti; X = Pd, Pt and Au alloys are considered impractical for large scale bulk structural application and the Ni-Mn based ternary alloys are also not feasible options due to their high brittleness [Van Humbeeck, 1999a]. In case of ferromagnetic Ni-Mn-Ga system, the base alloy stoichiometry is Ni_2MnGa and the transformation pathways and temperature in this system have been reported to be highly sensitive to even small compositional variations that move the alloy from its base stoichiometry [Lanska et al., 2004]. Similar to other Ni-Mn SMAs, the Ni-Mn-Ga alloys too are brittle in nature but owing to their ferromagnetic nature, the diffusionless transformation in this system can be controlled by applying a magnetic field and therefore these could be an attractive option in energy sector, solid state refrigeration [Mañosa et al., 2010; Pecharsky et al., 2003; Krenke et al., 2005], aerospace and automotive industries.

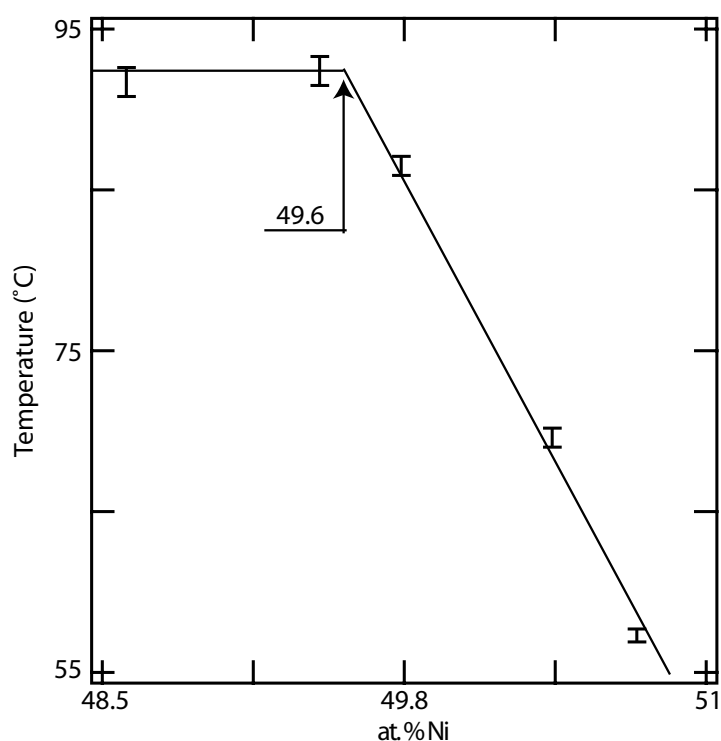


FIGURE 2.5: Effect of composition on transformation temperatures in NiTi, from [Funakubo \[1987\]](#) (Page 92)

2.4 NiTi based alloys

In a $\text{Ni}_{50}\text{Ti}_{50}$ alloy, ordered B2 austenite forms below 660 °C and exists as a line compound (Figure 2.1 [[Massalski et al., 1990](#)]) until it undergoes a diffusion transformation to martensite at sub 100 °C temperatures. The B2 phase therefore remains stable over a wide temperature range of $\approx 100 - 600$ °C. Various attempts have been made to date to render B2 unstable much earlier during cooling and therefore push the overall transformation regime to higher temperature by stoichiometric alloying. Addition of Au [[Huisman-Kleinherenbrink, 1991](#)], Hf [[Mulder, 1995](#)], Pd [[Huisman-Kleinherenbrink, 1991](#); [Delville et al., 2009, 2010](#)], Pt [[Huisman-Kleinherenbrink, 1991](#)], Rh, Zr [[Mulder, 1995](#)] have been observed to increase the TTs while even small amounts of Al, Fe, V, Cr, Co and Mn tend to reduce the TTs considerably [[Funakubo, 1987](#)](page 83).

Ternary and quaternary NiTi based HTSMAs are generally prepared by adding any one or an appropriate combination of the six elements mentioned earlier at the expense of primary elements Ni or Ti. While Pd, Pt and Au are preferred as replacement for Ni (*i.e.*, (Ni-X)Ti alloys), Hf and Zr are used to replace Ti (*i.e.*, Ni(Ti-X) alloys) [[Firstov et al., 2006](#)]. In ordered alloys nearest neighbour preference is critical to the existence of a certain phase, for example, Ni atoms in the B2 phase of equiatomic NiTi would prefer to be surrounded by Ti atoms or by substitutional atoms that are of similar size and electronic structure. Similarly, each Ti

atom would prefer to be surrounded by Ni or other atoms of identical size and nature. Even if these conditions are satisfied, there could still be a limitation over the extent to which a given primary alloying element can be replaced, because at higher concentrations the new alloying element could form stable compounds which may then lead to cessation in the alloys shape memory functionality. For example, it has been reported that Pd, Pt and Au could be used to even completely replace Ni in (Ni-X)/Ti alloys [Huisman-Kleinherenbrink, 1991] but on the contrary in Ni(Ti-X) alloys Zr, Hf or Zr+Hf may replace only a maximum of ≈ 20 at.% Ti.

In binary NiTi, increasing Ni content above 49.6 at.% reduces the TTs by order of ≈ 33 °C/at.% while the TTs remains unchanged in Ti rich alloys, Figure 2.5 [Funakubo, 1987](page 92). The necessity to remain in vicinity of a slightly Ti rich stoichiometry observed in binary alloys also extends to ternary NiTi based HTSMAs as follows. In case of ternary Ni(Ti-X) and (Ni-X)Ti alloys, the equivalent of binary Ni:Ti ratio is Ni:(Ti+X) and (Ni+X):Ti respectively. These ratios should be maintained in vicinity of 1:1 or even better if they reflect presence of > 50 at.% Ti or Ti+X in the microstructure. For example, in hot rolled $\text{Ti}_{50-x}\text{Pd}_{30}\text{Ni}_{20+x}$ ($x = -0.6$ to -1.5) alloys, Shimizu et al. [1998] reported a large drop in TTs of the order of ≈ 150 °C/at.% in alloys where the (Ni+Pd) fraction of the alloys exceeded ≈ 49.8 at.%, Figure 2.6. On the contrary, [Noebe et al., 2006] did not observe any excessive Ni related drop in TTs in (Ni-X)Ti type $(\text{NiPt}_{20})_x\text{Ti}_{100-x}$ ($x = 48$ to 52) alloys. In Ni(Ti-X) class $\text{Ni}_x\text{Ti}_{85-x}\text{Zr}_{15}$,

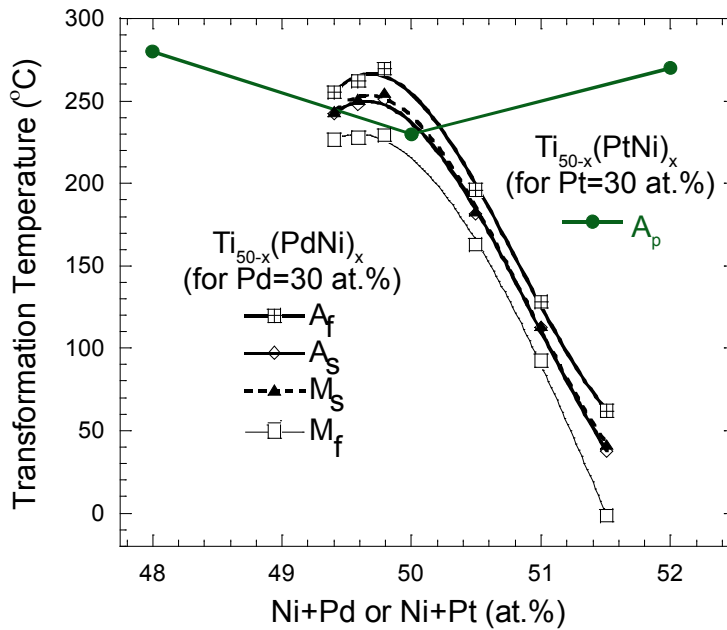


FIGURE 2.6: Effect of (Ni+Pd/Pt):Ti ratio on martensitic transformation temperatures, after Shimizu et al. [1998] and Noebe et al. [2006]. Here A_p is the peak austenite transformation temperature.

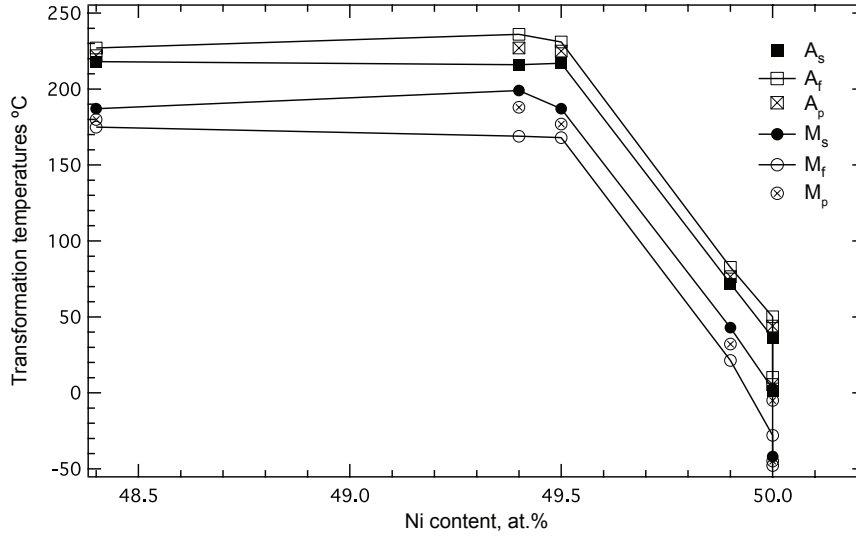


FIGURE 2.7: Effect of Ni content on transformation temperatures in $\text{Ni}_x\text{Ti}_{85-x}\text{Zr}_{15}$ alloy [Mulder, 1995].

($x = 48.4$ to 50.2) alloys excessive Ni related drop in TTs was reported by Mulder [1995]. These results are summarised in Figure 2.7 and the drop in the TTs were reported to initiate at ≈ 49.5 at.% Ni at a rate of ≈ 400 °C/at.%. In another investigation on Ni(Ti-X) alloys, AbuJdom et al. [1992] studied a series of $\text{Ni}_{40+x}\text{Ti}_{50-x}\text{Hf}_{10}$ ($x = 0$ to 10.5) alloys and observed a steep drop in TTs for Ni additions higher than ≈ 50 at.% Ni.

These results indicate the sensitiveness of TTs in NiTi based HTSMAs on stoichiometry and emphasize the importance of composition control during alloy making process.

2.4.1 Crystal structures and morphologies of precipitates in NiTi

In any given SMA, precipitation of second phases could take place during alloy manufacturing, thermal treatments, training or through thermo-mechanical cycling during its service life. They are known to play a critical role in the functionality stability of SMAs [Wagner et al., 2010]. In this section, crystalstructures of some of the most commonly observed precipitates in binary NiTi system are reviewed.

Ti₂Ni: The crystal structure of Ti₂Ni is reported to be cubic with F d 3 m spacegroup and a lattice parameters of $1.132 \text{ \AA}$ [Mueller and Knott, 1963]. Ishida et al. [1997] conducted a detailed evolutionary investigation of the precipitation behaviour in a Ti rich NiTi alloy and concluded that the orientation of Ti₂Ni precipitates in a given NiTi grain always remains unchanged and the matrix-precipitate interface remains semi coherent even at peak growth.

Ti₃Ni₄: These precipitates are reported to have a rhombohedral structure with 6.7 Å and 113.9° lattice parameters [Zou et al., 1996]. They are completely coherent during initial stages of growth but are rendered semi coherent during peak growth stages. The morphology is reported to be oval disk-like and they tend to precipitate with their habit plane parallel to the {111} plane of B2 [Tadaki et al., 1986].

Ti₂Ni₃: Surprisingly, these precipitate are metastable and they undergoes a transformation from a high temperature tetragonal structure with I4/mmm space group and lattice parameters $a = 3.095$ Å, $c = 13.595$ Å to a low temperature orthorhombic phase with Bbmm space group and lattice parameters $a = 4.398$ Å, $b = 4.370$ Å and $c = 13.544$ Å [Hara et al., 1997].

TiNi₃: These precipitates have hexagonal DO24 type ordered structure with $a = 5.101$ Å and $c = 8.307$ Å [Taylor and Floyd, 1950]

2.4.2 (Ni-X)Ti Alloys (X=Pd, Au and Pt)

The earliest and elaborate investigations in this class of alloys were performed by Huisman-Kleinherenbrnik [1991]. These alloys are based on NiTi-TiX intermetallic mutual solubility or in other words the overall alloying operates on the basis of formation of pseudobinaries [Eremenko et al., 1989]. Depending on the type of alloying element, the extent of mutual solubility between NiTi and TiX varies. In the present (Ni-X)Ti class with Pd, Au and Pt as ternary alloying options, for each ternary alloying element the resulting TiX intermetallic is entirely miscible in the B2 phase (NiTi intermetallic). Therefore, by appropriately controlling the stoichiometry as describe at the beginning of Section 2.4, it is possible to achieve TTs as high as 1000 °C [Huisman-Kleinherenbrnik, 1991; Van Humbeeck, 1999a; Firstov et al., 2006; Xu et al., 1997; Shimizu et al., 1998; Golberg et al., 1995]. Mechanistically, the equilibrium between NiTi and TiX facilitates early destabilisation of the B2 phase, therefore the complete transformation regime is pushed upwards and the martensite is rendered stable at a much higher temperature.

At least 10 at.% addition of any one of the three potential alloying elements is essential for a reasonable improvement in TTs but beyond this limit the rate of increase in TTs increases with the amount of third element addition. There is no maximum limit to which Ni can be replaced, even the equiatomic binaries, Ti-Pt, Ti-Au, and Ti-Pd [Quandt et al., 1996], formed by complete replacement of Ni from NiTi behave as SMAs. The effect of Pd, Pt and Au on M_s over the a complete range of composition is shown in Figure 2.8. The maximum increase in M_s is achieved by using Pt as the alloying element and least improvements are observed when Au is used. Below 10 at.% alloying addition, the M_s reduces slightly in all three cases, this also appears to be a common phenomenon in the Ni(Ti-X) class of alloys which are discussed

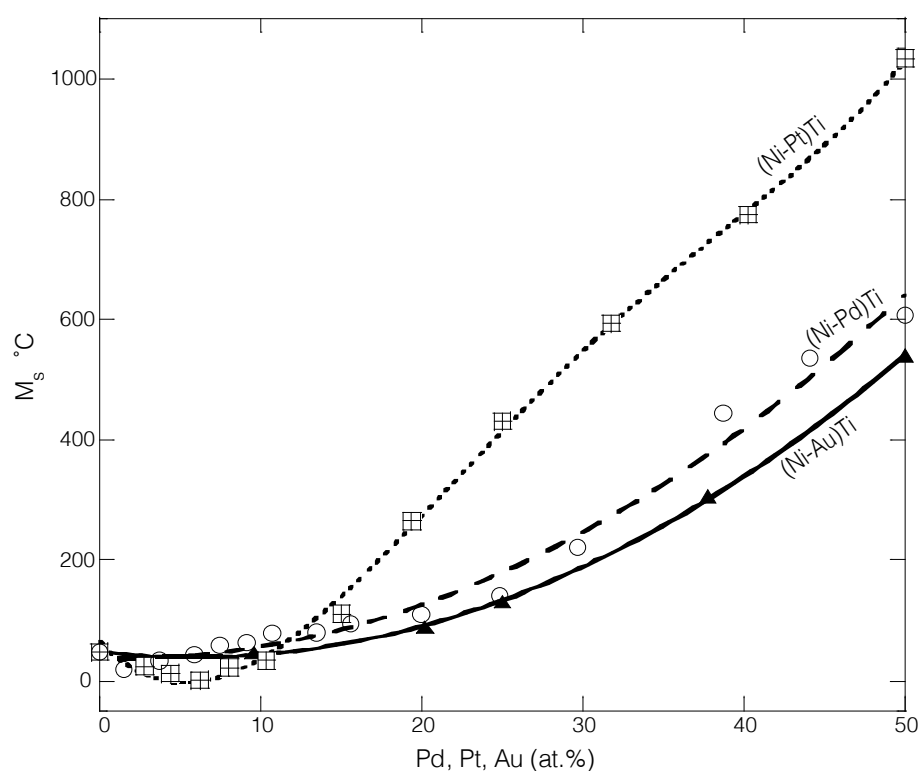


FIGURE 2.8: Effect of Pd, Pt and Au addition on M_s , in each case the elements were added at the expense of Ni while maintaining the equiatomic stoichiometry, after [Huisman-Kleinherenbrink \[1991\]](#).

in Section 2.4.3. In almost all the studies conducted to date on this class of alloys, a single step B2→B19 transformation has been reported [[Firstov et al., 2006](#); [Van Humbeeck, 1999a](#); [Mohanchandra et al., 2005](#); [Zhang et al., 2005](#); [Xu et al., 1997](#); [Shimizu et al., 1998](#)]. However, in some investigations on sputter deposited sub 8 at.% Pd thin films, a two step B2→R→B19' has been reported [[Zarnetta et al., 2007](#)].

One of the major difficulties in bulk structural applications of this class of alloys is the high cost of the alloying elements. Indicative cost comparison of the present class of HTSMAs with that of the Ni(Ti-X) class of alloys has been provided in Figure 2.9, adopted from [Mulder \[1995\]](#). Most of the current research in these alloys is therefore limited to thin films, for application in Micro Electro Mechanical Systems (MEMS) devices/actuators. These HTSMAs based MEMS devices, such as micro-valves [[Liu et al., 2004](#)], are being considered as potential candidates for weight critical applications in medical instrumentation or for actuation in hot fluid systems used in automotive and aerospace industry.

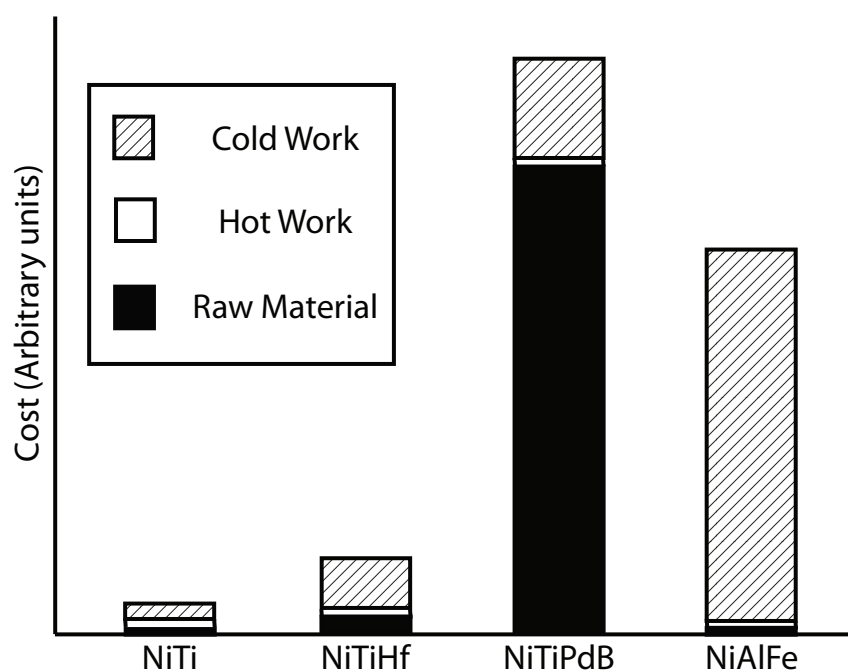


FIGURE 2.9: A relative estimate of the fabrication cost for four different SMAs, after [Mulder \[1995\]](#).

2.4.3 Ni(Ti-X) Alloys (X=Zr and Hf)

Like in (Ni-X)Ti, the Ni(Ti-X) class of alloys too are based on the mutual solubility of two intermetallic phases, in this case NiTi and the NiX, *via.* the formation of pseudobinaries [[Eremenko et al., 1989](#)]. In essence, a pseudobinary phase diagram is a constant pressure longitudinal (variable temperature) section of a ternary phase diagram parallel to one of the three faces that represents a true binary between any two of the three elements of the ternary system. In other words, it is an equilibrium diagram between two stoichiometrically similar phases. For example, in a Ni-Ti-Zr ternary system, an equilibrium diagram between NiTi and NiZr (the two stoichiometrically similar compositions) is considered as a pseudobinary phase diagram. A pseudobinary phase diagram may be isomorphous indicating of complete miscibility between the two intermetallics like in case of (Ni-X)Ti system where NiTi and TiX were completely miscible or they may contain multiple intermediate phases, often resulting from invariant reactions, such as in the case of current Ni(Ti-X) class of alloys. Therefore the two potential alloying elements Hf and Zr will have only limited solubility in NiTi and cannot replace the primary element Ti completely without a significant impact on the shape memory functionality. At 700 °C [Eremenko et al. \[1989\]](#) reported a maximum Hf and Zr solubility of ≈ 30 at.% in NiTi and at 500 °C they reported a maximum Hf solubility of 20 at.%.

Effect of Hf and Zr on transformation temperatures

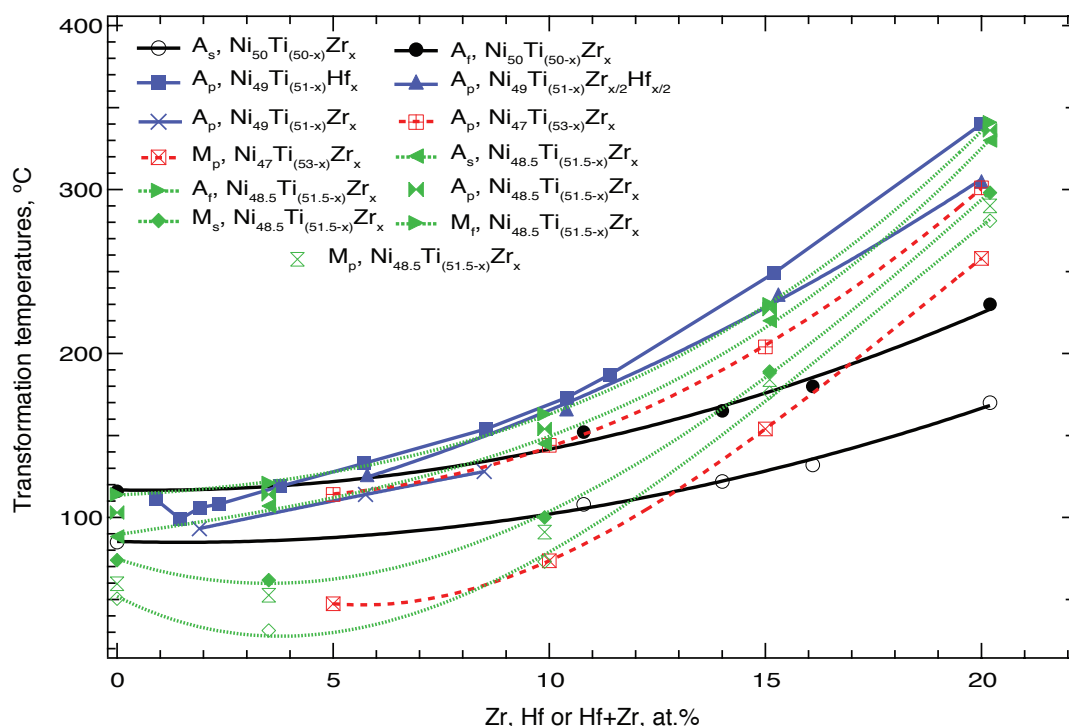


FIGURE 2.10: Effect of Hf, Zr and Hf+Zr addition on TTs, work done by Peterseim and Schlump [1992] is shown in black, AbuJudson et al. [1992] in blue, Hsieh and Wu [2000] in red and by Mulder [1995] in green.

The effect of Hf and Zr addition on TTs reported in various studies has been summarised in Figure 2.10. AbuJudson et al. [1992] observed a drop in peak austenite temperature (A_p) with Hf additions below 1 at.% and beyond this limit A_p was found to increase and the rate of increase in A_p also reported to increase gradually with addition of Hf. They observed a similar improvement in A_p when Hf and Zr were added together in equal amounts, exceeding 1 at.% in total, whilst adding Zr alone was found to produce a relatively lower improvement in TTs. Peterseim and Schlump [1992] studied the effect of Zr addition on TTs in the range of 10 to 20 at.%. They found that the improvement in TTs in the range of 10 to 14 at.% Zr was at the rate of ≈ 4 $^{\circ}\text{C}/\text{at.}\%$ and this rate was double in the range of 14 to 20 at.%. Hsieh and Wu [1998] reported a similar improvement in TTs with the addition of Zr in $\text{Ti}_{53-x}\text{Ni}_{47}\text{Zr}_x$ ($x = 5, 10, 15, 20$). In another investigation by Hsieh and Wu [2000] on quaternary $\text{Ti}_{50.5-x}\text{Ni}_{49.5}\text{Zr}_{x/2}\text{Hf}_{x/2}$ ($x = 0-20$ at.%) alloys, the authors reported an improvement in A_p from 50 to 320 $^{\circ}\text{C}$.

Potapov et al. [1997] used resistometry and X-Ray analysis to study the transformation in (Ti-Hf)Ni alloy and reported a maximum austenite temperature (A_f) of 322 $^{\circ}\text{C}$ for alloys containing 20 at.% Hf. Mulder [1995] reported a slightly different dependence of M_p on Zr addition in

$\text{Ni}_{48.5}\text{Ti}_{51.5-x}\text{Zr}_x$. Below 10 at.% Zr, while A_p increased fairly linearly, M_p reduced initially and then started increasing linearly beyond 4 at.% Zr. Beyond 10 at.% Zr addition, the rate of increase in TTs was relatively pronounced and a maximum A_p of $\approx 300^\circ\text{C}$ was reported by the author. Mulder [1995](page 84) also studied the effect of quaternary additions on TTs in

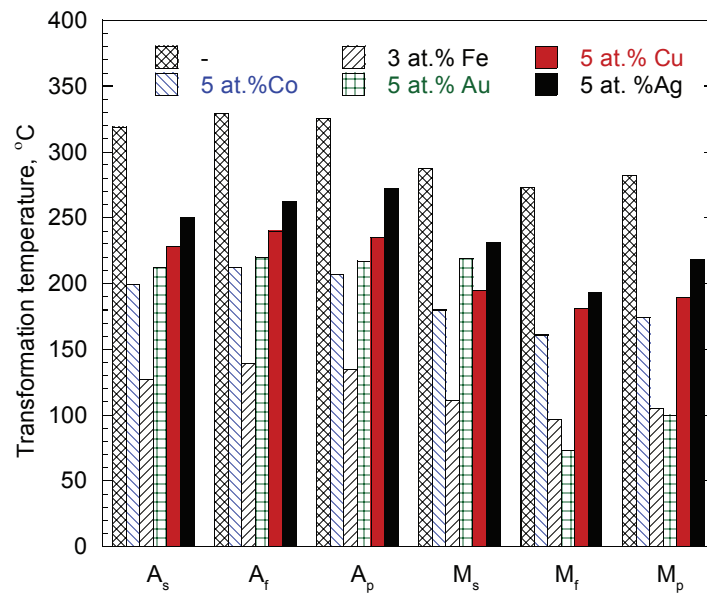


FIGURE 2.11: Effect of Co, Au, Cu, Ag and Fe (added at the expense of Ni) on transformation temperatures in Ni(Ti-Zr) based HTSMAs.

$(\text{Ni-X})_{48.5}\text{TiZr}_{20}$ ($X = \text{Co, Au, Cu, Ag, Fe}$), these are summarized in Figure 2.11. In all five alloys the author reported a considerable decrease in TTs. In alloys containing Cu and Fe the M_p decreased by ≈ 95 and 175°C respectively. Ag was reported to be nearly immiscible and the M_p in this particular alloy was found to decrease by $\approx 60^\circ\text{C}$.

In NiTi based SMAs the addition of Cu and Fe at the expense of Ni changes the transformation path by varying the thermal softening response of C' and C_{44} elastic constants [Ren et al., 2001] of the high temperature B2 phase but in the quaternary alloys studied by Mulder [1995], no such change in transformation path was reported.

Effect of Hf and Zr on lattice parameters and transformation pathways

$\text{Ni}(\text{Ti-X})$ ($X=\text{Hf, Zr}$) alloys undergo a single step transformation from $\text{B2} \rightarrow \text{B19}'$ [Firstov et al., 2006; Potapov et al., 1997]. Martensitic transformations are diffusionless and under an induced stress, the transformed (twinned) martensite detwins, adding to the pseudo elasticity. Twinning involves a co-ordinated sub-atomic movement of atoms and therefore any change in lattice parameter of the martensite affects not just the transformation thermodynamics but also the

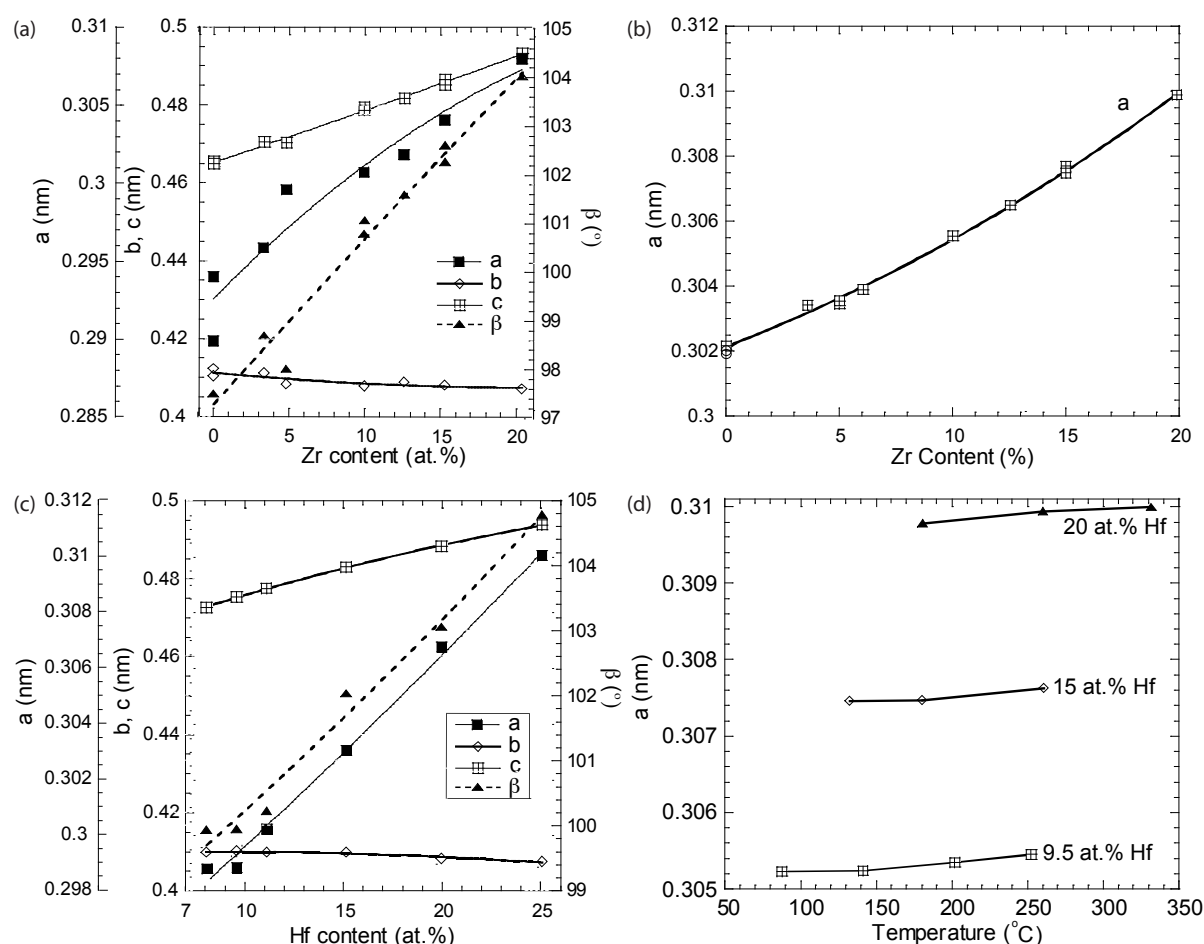


FIGURE 2.12: Effect of Hf addition on B19' and B2 lattice parameters are shown in (a) and (b) respectively. The effect of Zr addition on B19' and B2 lattice parameters are shown in (c) and (d) respectively. Note that for better visualization of B19' lattice parameters, three different Y-scales are used in figures (a) and (c).

twinning micromechanics. It is therefore essential to keep track of the changes in the lattice parameters with addition of alloying elements.

A detailed crystallographic study on Ni(Ti-Zr) alloys was done by Mulder [1995] and on Ni(Ti-Hf) by Potapov et al. [1997]. In the former investigation, the alloys were prepared by Vacuum Arc Melting(VAM) technique and in the latter they were produced by melt spinning. The results from these two studies is summarized in Figure 2.12, a linear increase in all B2 and B19' lattice parameters was reported, except for the 'b' parameter of the B19' which did not change significantly with addition of Hf or Zr. In Figure 2.12(d), the change in lattice parameter in three alloys, $\text{Ni}_{50}\text{Ti}_{(50-x)}\text{Hf}_x$ ($x = 9.5, 15, 20$ at.%).

Han et al. [1995] reported a single step B2→B19' transformation in $\text{Ti}_{36.5}\text{Ni}_{48.5}\text{Hf}_{15}$ alloy and they also claim to have observed amorphous regions in their vacuum arc melted alloy. Hsieh and

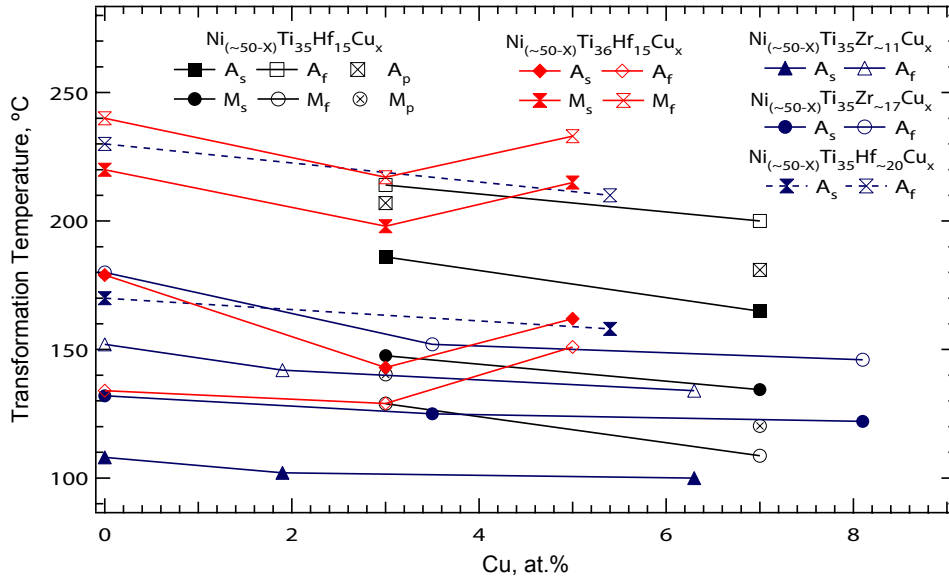


FIGURE 2.13: Effect of Cu on transformation temperatures, work done by [Meng et al. \[2002\]](#) is shown in black, [Liang \[2001\]](#) in red and by [Peterseim and Schlump \[1992\]](#) in blue.

[Wu \[2000\]](#) observed a single step $B2 \rightarrow B19'$ transformation in quaternary $Ti_{30.5}Ni_{49.5}Zr_{10}Hf_{10}$, they did not discuss the effect of Hf and Zr on the lattice parameters in detail. Current literature lacks a fundamental study that correlates the change in lattice parameter to the twinning behaviour of the martensite.

The addition of Cu at the expense of Ni in NiTi based SMAs has been shown to reduce the transformation temperature hysteresis by changing the transformation path from $B2 \rightarrow B19'$ to $B2 \rightarrow B19 \rightarrow B19'$ [[Nam et al., 1990](#)]. On similar grounds, the effect of Cu on transformation path and TTs in $Ni_{49-x}Ti_{36}Hf_{15}Cu_x$ ($x = 3, 5$) was investigated by [Meng et al. \[2002, 2005\]](#). The authors claimed to have observed a two step transformation *via* R-phase. Although, the Digital Scanning Calorimetry (DSC) data and X-ray Diffraction (XRD) spectra presented in their study showed a relative change with the addition of Cu, but their XRD analysis was not convincing enough to come to a strong conclusion about the presence of R-phase. Surprisingly, there was no significant change in TTs (Figure 2.13), a maximum drop of $\approx 20^\circ C$ was observed in an alloy containing 3 at.% Cu. A similar effect of Cu addition on TTs in Ni-Ti-Hf based alloys was reported by [Liang \[2001\]](#). [Peterseim and Schlump \[1992\]](#) studied a series of stoichiometric Ni-Ti-Zr based HTSMAs with varying Cu fractions, added at the expense of Ni. They reported a small drop in transformation temperature for Cu additions less than 8 at.%.

Phases and microstructures

The types of phases and their distribution plays an important role in stress or temperature induced transformations and the workability of alloys. A detailed study of the phases that appear after isothermal annealing (at 900°C) in $\text{Ti}_{53-X}\text{Ni}_{47}\text{Zr}_X$ ($X = 5, 10, 15, 20$) alloys was reported by [Hsieh and Wu \[1998\]](#) using a Electron Probe Micro Analyzer (EPMA) equipped Scanning Electron Microscope (SEM). After annealing at 900 °C for 72 hours, the authors reported dual and triple phase microstructure depending on the Zr content. The primary phase in all cases was (TiZr)Ni and the other two (secondary) phases were; Ti rich, $(\text{TiZr})_2\text{Ni}$ and Zr rich λ_1 (a Laves phase with a MgZn_2 type of structure). While both were observed in alloys containing 15, 20 and 25 at.% Zr, only $(\text{TiZr})_2\text{Ni}$ was observed in alloys containing 5 at.% Zr. The volume fraction of secondary phases varied depending on the Zr content but their distribution was such that they were always adjacent to one another. Further, using differential thermal analysis (DTA) and microstructural studies the authors have recorded three major events; melting of λ_1 phase at 930°C, reverse peritectic reaction: $(\text{Ti,Zr})_2\text{Ni} \rightarrow (\text{TiZr})\text{Ni}$ at 990°C and finally the melting of (TiZr)Ni at 1160°C. The maximum temperature for hot workability of these alloys is therefore limited by the λ_1 melting point, i.e., 930°C.

Elastic strain recovery

The elastic/pseudoelastic strain recovery (e_{elr}) and temperature hysteresis are the two other factors that play key roles in large scale implementation of SMAs as structural candidates in aerospace and automotive industries. Addition of Hf and Zr increases the TTs but on the downside they tend to reduce the overall transformation strain. So far only a maximum of 3% [[Meng et al., 2000](#)] complete recovery is reported in Ni(Ti-X) class of alloys, much lower in comparison to a $\approx 8\%$ often reported in near equiatomic binary NiTi [[Funakubo, 1987](#)](page 177).

[Meng et al. \[2000\]](#) reported a 3% strain recovery, TWSME and a martensite start (M_s) and finish (M_f) temperatures of 125 and 180°C respectively in homogenized (at 950°C for 1.5 h) and rolled $\text{Ti}_{36}\text{Ni}_{49}\text{Hf}_{15}$ alloy. The authors used an unconventional technique to quantify the SMF; a cantilever type bending strain was applied and the extent of spring back was interpreted as shape recovery during transformation. For a 2.5% bending strain, they reported a 100% strain recovery after heating the sample above A_f whilst for a 4.5% strain the recovery was only 91%. Further, the temperature at which the strain was induced had a marked effect on recovery. For example, a 3 % strain induced at 20°C could be recovered completely by heating the sample above A_f but a same strain induced at 100°C resulted in only 92% recovery. The authors have

attribute this to the competition between twin based and slip based deformation mode and put forth following explanation. Beyond a certain temperature the dislocation movement becomes thermodynamically more favourable than twinning events and therefore there is some amount of plastic deformation invariably associated with the transformation related twinning events at higher temperatures and therefore the low strain recovery. The TWSMF was induced by ageing the samples at 700°C for 10, 20, 40, 80 and 120 respectively. Unlike one way SMF, the stability of TWSMF was reported to be poor.

In a comparative study between a quaternary $\text{Ti}_{50.5-x}\text{Ni}_{49.5}\text{Zr}_{x/2}\text{Hf}_{x/2}$ and ternary $\text{Ni}(\text{Ti-Zr})$ HTSMAs, by [Hsieh and Wu \[2000\]](#), the quaternary alloy exhibited relatively better shape recovery properties than ternary. None of the investigations conducted to date on these alloys explain the micro-mechanics governing the shape recovery response. An understanding of the effect of alloying additions, deformation temperature and thermal cycling on micro mechanics is necessary for development of new and more advanced NiTi based HTSMAs of this class.

Effect of ageing and thermo mechanical treatments on transformation

Martensitic transformations in NiTi based SMAs are highly sensitive to cold working, ageing or annealing and thermo-mechanical treatments. Any reduction in thermal hysteresis is advantageous in designing precise actuators[Ref.]. Apart from thermal hysteresis, another primary requirement for successful implementation of a high temperature shape memory alloy is its thermal stability.

[Hsieh and Wu \[2000\]](#) presented a detailed account of the effect of ageing (at 285°C for upto 50 days), cold rolling (in the range of 5-25%) and thermal cycling on transformation temperature in quaternary $\text{Ti}_{50.5-x}\text{Ni}_{49.5}\text{Zr}_{x/2}\text{Hf}_{x/2}$ ($x = 0-20$ at.%) alloys. In their work, cold working resulted in an improvement in transformation temperature significantly but it dropped abruptly within a few thermal cycles and remained constant there after. For example, after 10% cold work, A_p reduced from 341°C in first heating cycle to about 190°C in the second. This behaviour is often termed as 'mechanically induced martensite stabilization', present literature lacks a clear mechanistic explanation to this response. Further in the same work, the authors observed an increment in hardness of the as-cast and homogenized alloy during thermal cycling. With this increase hardness, there was a simultaneous decrease in TTs, at a relatively higher rate in first 10 cycles and at a much lower rate afterwards. This increase in hardness and decrease in TTs was attributed to the difference in the volume change between the transforming matrix and the non-transforming secondary phases. The interface/grain boundaries between the matrix and the secondary phases therefore act as dislocation source during thermal cycling. The authors reported an increase in hardness by about 25% in just 100 cycles. It is further suggested that

the complex stress field that develops during this process, impedes the forward, $B2 \rightarrow B19'$ transformation during cooling. The residual stresses developed after forward transformation during that particular cycles then accelerates the $B19' \rightarrow B2$ transformation during heating. Hence the transformation temperatures decrease and the temperature hysteresis increases marginally. Ageing the alloy below peak $B19' \rightarrow B2$ transformation temperature (A_p) had a minimal impact on the transformation behaviour. This investigation clearly show the detrimental effect of some of the common processes like cold working on the martensitic transformations, current literature lacks a clear mechanistic explanation to this response.

Mulder [1995] observed a pronounced effect of ageing on thermal cycling in $Ni_{48.5}TiZr_{20}$ alloy (homogenized at $880^\circ C$ for 48 hrs). In un-aged state the alloy showed a continuous drop in TTs during thermal cycling. Ageing at $290^\circ C$ ($35^\circ C$ below the A_s) for 2 hours did not alter the thermal cycling behaviour considerably. On the other hand, ageing in austenitic state (at $350^\circ C$) for an hour resulted in a large drop in TTs but the alloy was stable and there was no drop in TTs during thermal cycling. These results show that there is a considerable effect of dislocation activity on martensitic transformations in these alloys. A detailed in situ investigation (using techniques like synchrotron diffraction) of micro events happening during transformation is therefore necessary to understand the micro mechanics of transformation in these alloys.

The temperature induced transformation hysteresis (or in other words thermal hysteresis) gives indication of the amount of energy that is dissipated in the alloy due to lattice frictional forces during the transformation. Mulder [1995] (page 72) reported an increase in thermal hysteresis in $Ni_{48.5}Ti_{51.5-x}Zr_x$ (Refer Figure 2.10) alloys for Zr additions below 10 at.% and in the range of 10 to 20 at.% Zr, there was a considerable decrease but it occurred at a very slow rate. In NiTi based SMAs, addition of Cu at the expense of Ni changes the transformation path from $B2 \rightarrow B19'$ to $B2 \rightarrow B19 \rightarrow B19'$ Nam et al. [1990]. A major advantage of this change in transformation route is the reduced thermal hysteresis associated with the $B2 \rightarrow B19$ transformation step. For example, the thermal hysteresis associated with $B2 \rightarrow B19'$ transformation in binary NiTi is in the range of $50-60^\circ C$ Otsuka and Ren [2005] (Page-525) while it's only a mere $11^\circ C$ for $B2 \rightarrow B19$ transformation in $TiNi_{40}Cu_{10}$ Nam et al. [1990]. In an effort to reduce the transformation hysteresis in HTSMAs, Peterseim and Schlump [1992] studied the effect of copper on transformation temperature in a series of Ni-Ti-Zr alloys, Zr and Cu were added at the expense of Ti and Ni respectively. The authors observed a single step $B2 \rightarrow B19'$ transformation and a slight reduction in thermal hysteresis, refer Figure 2.13. The effect of Cu on thermal hysteresis and overall transformation temperatures was relatively pronounced in alloys containing Zr more than 16 at.%. On the other hand, in Ni(Ti-Hf) based alloys, addition of Cu at the expense of Ni in the range of 1-5 at.% resulted in a minimal change in thermal hysteresis [Meng et al., 2002],

refer Figure 2.10. Further investigation in such alloy systems is necessary to evaluate the exact role of elements like copper in micro mechanics of transformation.

In ending, this critical review on Ni(Ti-X) HTSMAs shows that there exists a very elusive understanding of the transformation micro-mechanics. Elaborate studies using techniques like synchrotron diffraction are therefore necessary to gain an in-depth knowledge of micro-mechanics operating in these alloys. The understanding of micro-mechanics will accelerate the development of these alloys by making the alloy designing process more systematic. Literature review on Zr-Cu-Co-Ni and Ni-Mn-Ga alloys have been provided in Chapters 4 and 5 respectively.

Chapter 3

Ni(Ti,Hf,Zr)-based High Temperature Shape Memory Alloys

Summary

Fine grained polycrystalline NiTi shape memory alloys containing 15 at.% Hf and Zr and zero or 3 at.% Cu fabricated by ingot metallurgy were examined using in situ synchrotron X-ray diffraction in order to examine the viability of producing affordable high temperature shape memory alloys. The alloys produced had a high thermal hysteresis, in excess of 70 °C but A_f temperatures of over 250 °C were obtained for $Ni_{50}Ti_{35}Hf_{15}$. 3 at.% Cu additions did not significantly reduce the per-cycle degradation of TTs but did reduce the TTs. The evolution of the lattice parameters during the first five thermal cycles was observed. Negative thermal expansion was found in the $b_{B19'}$ cell direction in all the alloys examined and significant deviations in the lattice parameters in the region of transformation were found. A per-cycle evolution in the end-point B19' lattice parameters was observed, but no such evolution was found for the B2 phase, which is rationalised by appealing to the production of a population of interface dislocations.

3.1 Introduction

Shape memory alloys operate by a martensitic, long-range diffusionless transformation from one crystal structure to another; the transformation may be superelastic or it may be temperature induced. In the former case, they are of utility as low modulus, high strain springs and in the latter as thermal actuators. They are also used as one-time devices to provide a deployable structure *via.* the remarkable martensite memory phenomenon, for example in space craft.

In the actuator application, it is desirable to possess HTSMAs with much higher actuation temperatures that would be applicable to, for example, gas turbine compressor ducts and noise suppression systems [Birch and Webster, 2006; Calkins et al., 2006; Hartl and Lagoudas, 2007].

Regular near-equiatomic NiTi has TTs in the range of 0 to 20 °C for the on-cooling transformation and 30 – 80°C for the on-heating transformation, by Liu et al. [1997]. The existence of a hysteresis in the TTs must be due to the presence of non-recoverable defects, such as interface dislocations, since purely elastic and thermodynamic contributions to the driving force would result in a fully reversible transformation. Indeed, when the interface strain is minimised according to the phenomenological theory of martensitic transformation, the hysteresis is also minimised [Cui et al., 2006].

There are three common approaches to altering the TTs; (i) varying the Ni:Ti stoichiometry within the narrow range possible for the NiTi phase [Funakubo, 1987; Tang, 1997], (ii) by intentional or unintentional interstitial alloying with, *e.g.* C [Funakubo, 1987; Frenzel et al., 2007] or (iii) by stoichiometric addition of ternary [AbuJdom et al., 1992; Huisman-Kleinherenbrnik, 1991; Mulder, 1995; Van Humbeeck, 1999a; Firstov et al., 2004; Zarinejad et al., 2008] or quaternary [AbuJdom et al., 1992; Van Humbeeck, 1999a; Mulder, 1995] alloying elements. Approach (i) is difficult to deploy in industrial practice, because it requires finer control of the Ni:Ti ratio in the melt than can readily be achieved, drastic reduction in TTs is observed in alloys with higher Ni content. Approach (ii), additions of carbon or oxygen does not have a direct effect on TTs, rather both elements preferentially combine with Ti to form stable compounds leaving the matrix Ni rich and therefore resulting in reduction in TTs [Funakubo, 1987]. The restriction over compositional stoichiometry to remain in vicinity of equiatomic composition observed in binary NiTi is also extended to certain NiTi based ternary alloys [Xu et al., 1997; Noebe et al., 2006] *via.* the formation of pseudo binaries, Noebe [2005]. Therefore, in ternary and quaternary alloy (approach iii) it is desirable to maintain the (Ni,X₁):(Ti,X₂) ratio in vicinity of 1:1, where X₁ and X₂ are third and/or fourth element substitutions for Ni and Ti respectively. Most substitutions for Ni, *e.g.* with Co, Fe or Cr lead to reductions in TTs, whereas substitution of Hf or Zr for Ti have been observed, at least by differential scanning calorimetry, to lead to an increase in TTs. Alternatively, Pt [Huisman-Kleinherenbrnik, 1991], Pd [Huisman-Kleinherenbrnik, 1991; Delville et al., 2009, 2010] or Au [Huisman-Kleinherenbrnik, 1991] substitutions for Ni are attractive, but these are unlikely to be economically viable except for niche low volume applications such as thin films or in space crafts.

A major problem for the widespread deployment of practical SMA actuator is functional stability; frequently it is observed that the TTs and strain evolve on repeated, thermomechanical [Eggeler et al., 2004; Ma et al., 2010] or even just thermal cycling under a constant load [Jones and Dye, 2011]. The prospect is raised of either an impaired fatigue response or of the on-cooling

transformation dropping below the ambient temperature of the device environment, and hence cessation of function. It is usually felt that this evolution is due to build up of defects, such as dislocations produced at the martensite-austenite interface [Hamilton et al., 2004]. In a Cu based SMAs dislocations have even been observed to serve as heterogeneous martensite nucleation sites [Ibarra et al., 2007]. Further to this, Simon et al. [2010] observed multiplication of dislocations in NiTi single crystals during thermal cycling. These studies emphasise the importance of defects in SMAs. Therefore much research has focussed on mechanical processing to provide a stable defect population, *e.g.* by the production of a very fine grain size and/or by the introduction of additional stable intermetallics such as, TiNi_3 [Taylor and Floyd, 1950], Ti_2Ni [Mueller and Knott, 1963] and Ti_3Ni_4 [Tadaki et al., 1986; Khalil-Allafi et al., 2002], although a clear mechanistic understanding of the role of defects and their evolution during transformation is still elusive.

In binary NiTi alloy, the high temperature phase is found to be the B2 ordered *bcc* structure and the low temperature phase is usually found to be produced by an orthorhombic distortion and shear of the B2 phase to a monoclinic B19' [Otsuka and Ren, 2005], but other related crystal structures are also possible. For example, Cu additions in near-equiatom NiTi are observed to promote a two-step transformation from the B2 phase to an orthorhombic B19 and then shear to the monoclinic B19' structure for Cu additions in excess of 9 at.% [Miyazaki and Ishida, 1999]. Such two-step transformation paths are supposed to lead to enhanced stability, by providing fewer habit plane variant (HPV) possibilities.

Much of the existing literature is confined to ternary additions and provides only macroscopic symptomatic extensive property data such as that provided by dilation or calorimetry. Such approaches are appealing on economic grounds but provide only limited insight into the evolution of the material as the transformation proceeds, into the nature of the interface plane or into the way in which the transformation strains are accommodated by elasticity when a two phase mixture is present.

In this chapter the transformation behaviour of $\text{Ni}_{50}\text{Ti}_{35}\text{X}_{15}$ alloys with and without the substitution of 3 at.% Cu for Ni, where X= Hf or Zr is examined. Hf and Zr additions are attractive because both have reasonable solubility in NiTi [Semenova and Tret'yachenko, 2001], because they do not possess very high density and because their cost is moderate. Synchrotron X-ray powder diffraction is employed to examine the transformation behaviour, except in case of $\text{Ni}_{47}\text{Ti}_{35}\text{Zr}_{15}\text{Cu}_3$, on repeated no-load thermal cycling and the diffraction elastic constants of each phase, providing a first estimate of the effect of alloying on the single crystal properties.

3.2 Experimental Description

The alloys were prepared by Vacuum Arc Melting (VAM) 3N or higher purity constituent elements (in Ar), taken in lump or sponge form with maximum size of each varying between ~ 5 and 7 mm. Small ~ 50 g ingots were melted and remelted 5-6 times with inter-melt flipping followed by homogenization at 900°C for 24 h. They were then encapsulated in steel cans and hot rolled to a thickness of 3 ± 0.5 mm at 900°C in order to produce a fine grained microstructure so as to obtain complete Debye-Scherrer rings, Figure 3.1a, during Synchrotron X-ray diffraction (SXRD). Intact $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$ and $\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$ rolled strips were produced but cracking was observed in the $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ alloy.

The sXRD experiments were performed in transmission mode, Figure 3.1b, at the ID15B monochromatic beamline at the ESRF, France. The incident beam wavelength was $0.1427 \text{ \AA}$ and a Pixium 4700 [Daniels and Drakopoulos, 2009] area detector mounted at a distance of 1.228 m from sample was used to record complete Debye-Scherrer patterns. Polished flat dog-bone specimens with gauge $1.5 \times 1.5 \times 15$ mm in size were electro-discharge machined, except for $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ where a $1.5 \times 1.5 \times 8$ mm gauge stick specimen was used due to the unavailability of large intact uncracked sample lengths after rolling. An Instron electro thermo-mechanical testing (ETMT) machine was used for resistance heating and accurate temperature measurements were ensured by mounting an R type thermocouple on the top surface of the gauge volume of the X-ray beam; the beam was used for alignment. To ensure good electrical contact at grips, a small load of 5 MPa was applied during thermal cycling.

Using a 0.5×0.6 mm beam adequate diffraction images could be obtained in 0.4 s during heating and cooling at a rate of 1°Cs^{-1} . Intensity (integrated around 360° azimuthal angle) *vs.* diffraction angle (2θ) patterns, Figure 3.1c, were obtained from the 2D images by using FIT2D [Hammersley et al., 1996]. A ceria standard was used to calibrate the diffractometer. Each pattern was Rietveld [1969] refined using the Generalized Structure Analysis System (GSAS) [Larson and Von Dreele, 1994; Toby, 2001] to evaluate the lattice parameters and volume fractions of each phase. The strong rolling texture produced, which evolved during the experiments, meant that a model texture was refined during Rietveld fitting; χ^2 of less than 1 were obtained in the majority of cases. The atomic positions obtained for B19' were consistent with those reported by Cuevas et al. [2006].

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 822^e instrument using Aluminium as a reference. Heating and cooling was performed at a rate of 10°Cs^{-1} in nitrogen gas environment. Large area EDX measurements were performed in an SEM to obtain the alloy compositions actually achieved.

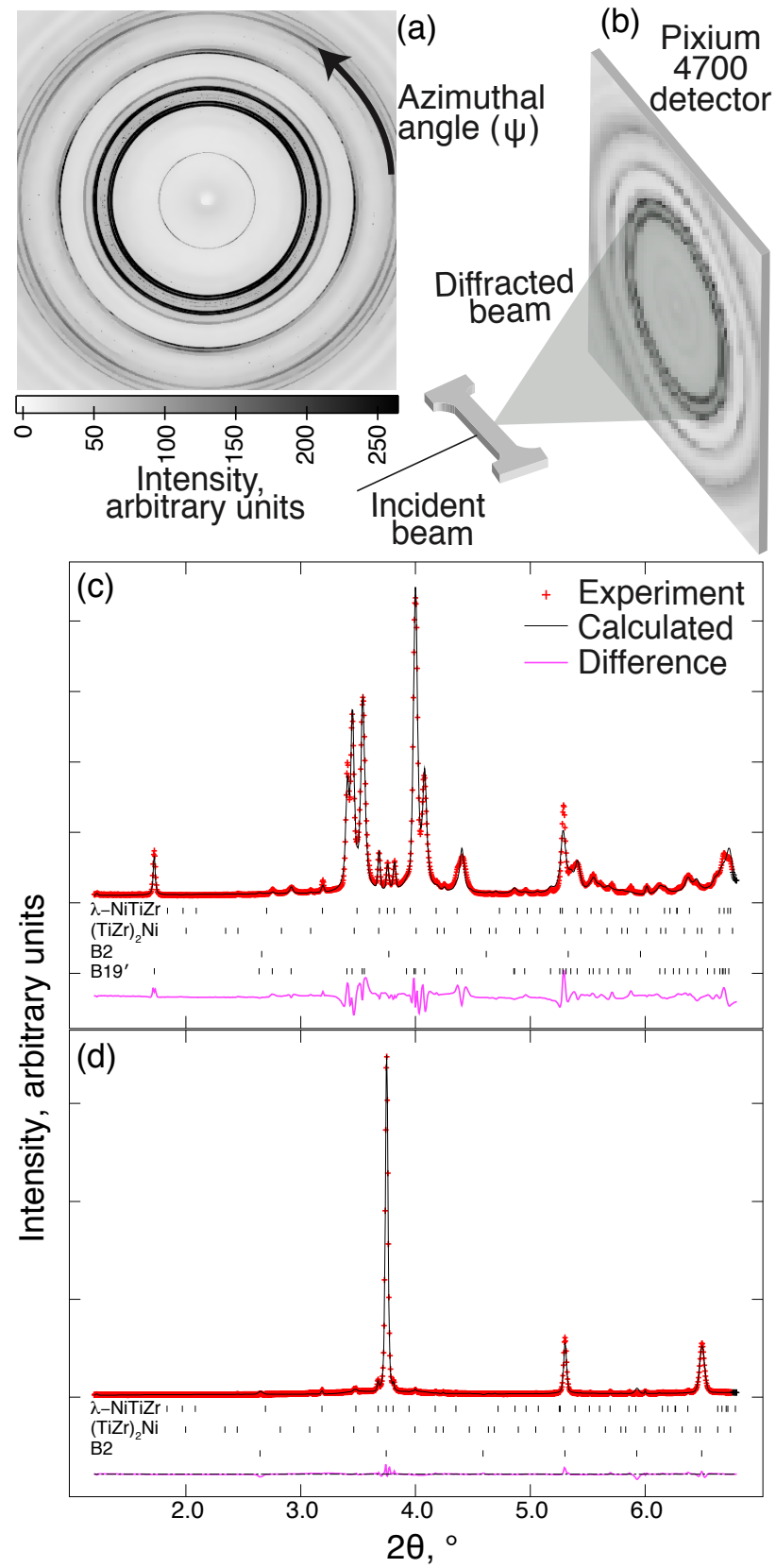


FIGURE 3.1: (a) diffraction pattern at 0% strain showing B19' rings in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ HTSMA, (b) Synchrotron X-ray diffraction experimental setup and (c) X-ray diffraction spectra; integrating intensity across complete diffraction ring

TABLE 3.1: Average matrix compositions measured using EDX (at.%) for each alloy examined.

	Ni ₅₀ Ti ₃₅ Hf ₁₅	Ni ₅₀ Ti ₃₅ Zr ₁₅	Ni ₄₇ Ti ₃₅ Hf ₁₅ Cu ₃	Ni ₄₇ Ti ₃₅ Zr ₁₅ Cu ₃
Ni	49.7	49.5	47.0	46.2
Ti	35.0	36.8	36.4	36.3
Hf	15.3	—	14.2	—
Zr	—	13.7	—	14.8
Cu	—	—	2.5	2.7

TABLE 3.2: TTs in the alloys examined. The top section lists the first cycle temperatures evaluated using DSC and the bottom section lists the temperatures for all five thermal cycles evaluated using sXRD, all in °C

DSC	Ni ₅₀ Ti ₃₅ Hf ₁₅	Ni ₅₀ Ti ₃₅ Zr ₁₅	Ni ₄₇ Ti ₃₅ Hf ₁₅ Cu ₃	Ni ₄₇ Ti ₃₅ Zr ₁₅ Cu ₃
M _s	212	201	146	130
M _p	204	169	134	115
M _f	188	125	124	97
A _s	249	195	178	161
A _p	254	225	190	183
A _f	257	238	197	196
A _f – M _f	69	113	73	99

sXRD		Cycle1	Cycle2	Cycle3	Cycle4	Cycle5
Ni ₅₀ Ti ₃₅ Hf ₁₅	M _s	189	186	185	179	178
	M _f	135	129	127	127	125
	A _s	201	198	184	178	165
	A _f	240	234	233	231	228
	A _f – M _f	105	105	106	104	103
Ni ₅₀ Ti ₃₅ Zr ₁₅	M _s	201	197	192	188	183
	M _f	122	102	100	92	88
	A _s	201	186	186	171	165
	A _f	251	248	249	242	243
	A _f – M _f	129	146	149	150	155
Ni ₄₇ Ti ₃₅ Hf ₁₅ Cu ₃	M _s	137	133	129	126	125
	M _f	85	81	77	76	75
	A _s	140	131	116	113	113
	A _f	189	182	177	177	174
	A _f – M _f	104	101	100	101	99

3.3 Results and Discussion

The average matrix compositions of matrix of each alloy measured using Energy Dispersive X-ray Spectroscopy (EDX) are provided in Table 3.1. Invariably a small amount of $(\text{Ti,X})_2\text{Ni}$ ($\text{X}=\text{Hf}$ or Zr) phase was observed in all alloys and an additional Laves phase, λ was observed in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ [Majzoub et al., 2003], Figures 3.1c and 3.2. Precipitation of these additional phases during solidification and/or homogenization will have altered the matrix stoichiometry from the desired $(\text{Ti,X}):(\text{Ni,Cu})$ ratio of 1. This variation was of the order of $\approx 1.5\%$ in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ and $\text{Ni}_{47}\text{Ti}_{35}\text{Zr}_{15}\text{Cu}_3$ but was much lower in alloys with the Hf addition, implying that Hf widens the NiTi phase field and/or reduces on-solidification partitioning of Ti.

The DSC response of the homogenized and rolled alloys is presented in Figure 3.3. The first cycle TTs for each of the alloys are given in Table 3.2. $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$ showed the highest TTs, with an M_f in excess of 185°C . Zr additions were less effective and resulted in alloys with greater transformation hysteresis and a larger temperature range over which transformation occurred. Cu additions resulted in a quite appreciable reduction in the TTs, on the order of 70°C for the forward (heating) transformation and 60°C for the reverse transformation. Significant reductions in TTs were observed in all four alloys with thermal cycling; on the order of $3 - 6^\circ\text{C}/\text{cycle}$. The exo- and endothermic DSC peaks in the initial cycles are visibly asymmetric, suggesting that the rate of formation of last martensite is retarded compared to the first martensite. This and the broadening of the peaks seen on cycling is suggestive of an evolution of the defect structures (*e.g.* interface dislocations) in the material.

Monoclinic $\text{P}2_1/\text{m}$ cells can be expressed either in a so-called β [Otsuka et al., 1971] or a γ [Michal and Sinclair, 1981; Huang et al., 2003] crystal setting; the γ setting is used here, consistent with Hahn [2005]. Figure 3.2 is a panoramic view of the transformation sequence for the first thermal cycle of $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$. Individual diffraction patterns here are obtained by 360° angular integration of complete Debye-Scherrer rings (Figure 3.1a), each pattern representing the state of the alloy at a specific temperature. Initially in the cold condition the alloy is chiefly composed of $\text{B}19'$ with no presence of phase. On heating, the (101) $\text{B}19'$ peak drifts approximately linearly from the (020) $\text{B}19'$, presumably as a result of anisotropic thermal expansion. Then, during transformation appearance of the main $\{110\}$ $\text{B}2$ peak is observed; followed by its redissolution on cooling and restoration of the $\text{B}19'$ diffraction pattern. Because of the low background and divergence achieved using this instrument, the different $\text{B}19'$ peaks can be clearly discerned.

sXRD studies were conducted on all four alloys but the diffraction information on $\text{Ni}_{47}\text{Ti}_{35}\text{Zr}_{15}\text{Cu}_3$ could not be included here due to inaccuracies in temperatures recorded during



FIGURE 3.2: Evolution of the diffraction patterns during a complete heating and cooling cycle in $Ni_{50}Ti_{35}Zr_{15}$, showing the minor phases observed and the main $B2 \leftrightarrow B19'$ transformation

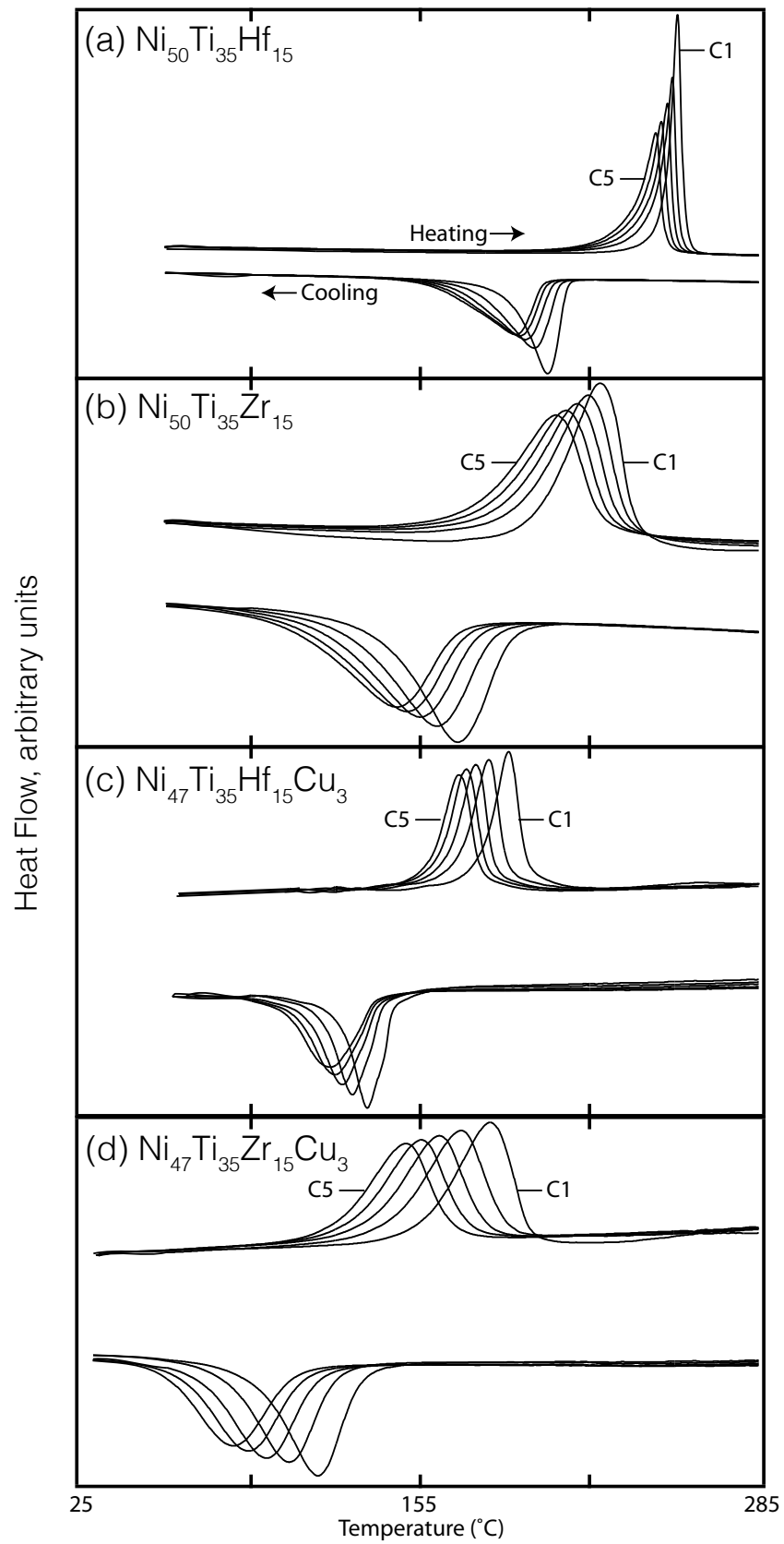


FIGURE 3.3: Differential Scanning Calorimetry results obtained for five heating and cooling cycles in the as-rolled alloys.

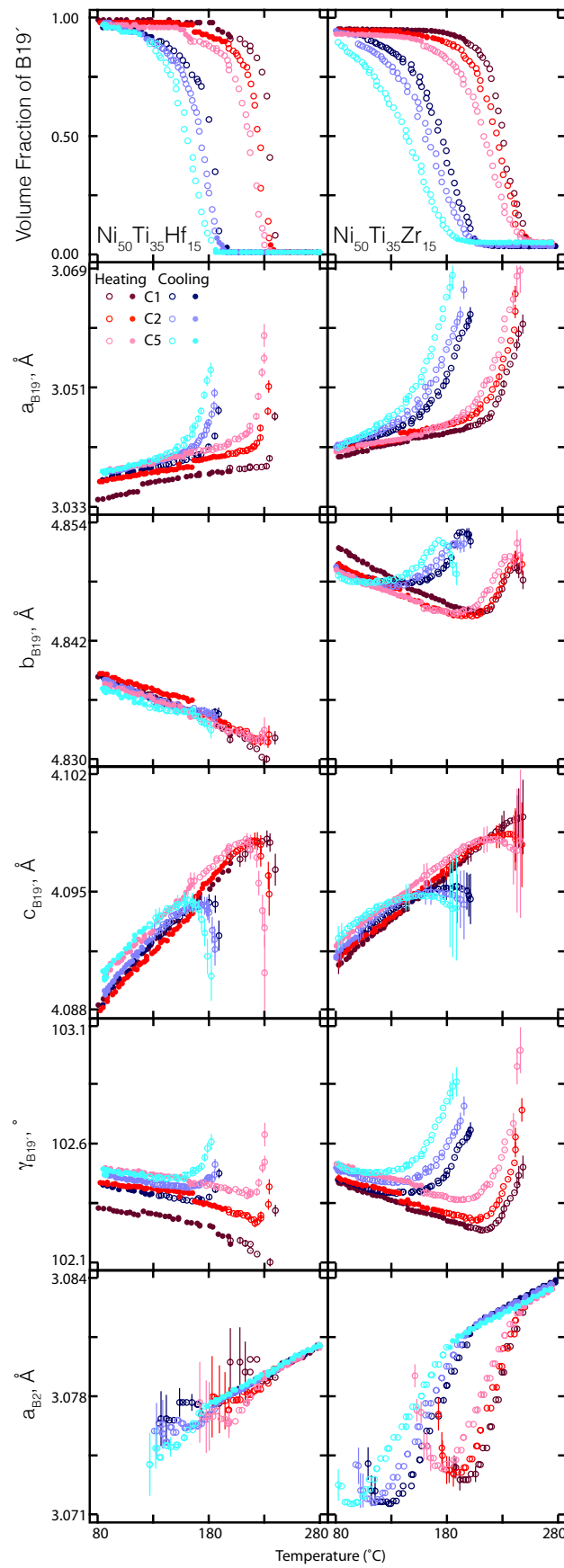


FIGURE 3.4: Lattice evolution in $Ni_{50}Ti_{35}Hf_{15}$ and $Ni_{50}Ti_{35}Zr_{15}$. Solid symbols are in single phase region and open symbols during transformation.

in situ thermal cycling on that alloy. The evolution of the Rietveld refined phase fractions and cell parameters in the $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$ and $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ alloys is shown in Figure 3.4. It is observed that the transformation proceeds more gradually in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ than in $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$, and that there is greater per-cycle drift, as observed in the DSC measurements. The TTs measured using the fitted diffraction data (at 10 and 90 wt.%) are also provided in Table 3.2. The temperatures obtained using sXRD will be less reliable than in DSC, because the heating arrangements are less isothermal using resistance heating than in a DSC, but most probably the transformation onset and completion can be measured more reliably; therefore a larger hysteresis is measured using diffraction but the absolute temperatures show slightly greater scatter. The fifth cycle austenite transformation interval ($A_f - A_s$) is 63 °C in $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$ and 78°C in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$, while the hysteresis ($A_f - M_f$, Table 3.2) is also greater in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ than in $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$. Previously, this has been correlated to the interface plane strain [Delville et al., 2010, 2009; Cui et al., 2006].

The $\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$ alloy, in contrast, shows almost the same interval and hysteresis as the Cu-free Hf alloy, but with lower TTs. The DSC results also show a lack of improvement in hysteresis with Cu additions. The drift on cycling was also similar in the two alloys. These results suggest that, at least at this level of doping, Cu additions do not improve the functional stability of the alloy.

The Rietveld refined room temperature lattice parameters of $B19'$, the B2 lattice parameter at 280 °C and the corresponding unit cell volumes are listed in Table 3.3. Compared to binary near equiatomic NiTi [Jones and Dye, 2011; Otsuka et al., 1971], $a_{B19'}$, $b_{B19'}$ and γ are larger, but $c_{B19'}$ is smaller. Of all three alloys, $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ has the largest $B19'$ unit cell and $\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$ has the largest B2 unit cell. The lattice parameters of both phases in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ are larger than that in $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$, in spite of the fact that the atomic radii of

TABLE 3.3: Rietveld refined unit cell parameters (in Å except for γ in degrees) and cell volumes (in Å³), at room temperature for $B19'$ and at 280°C for B2 in $\text{Ni}_{35}\text{Ti}_{50}\text{Hf}_{15}$, $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ and $\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$ are presented here. The near equiatomic NiTi lattice parameters adopted from Otsuka et al. [1971] are also tabulated here in a γ monoclinic angle setting for comparison.

The uncertainties are provided in parentheses.

	NiTi	$\text{Ni}_{35}\text{Ti}_{50}\text{Hf}_{15}$	$\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$	$\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$
$a_{B19'}$	2.889	3.0321(3)	3.0382(4)	3.0369(4)
$b_{B19'}$	4.622	4.8408(5)	4.8548(5)	4.8191(7)
$c_{B19'}$	4.120	4.0826(4)	4.0872(3)	4.0988(3)
$\gamma_{B19'}$	96.8	102.40(1)	102.51(1)	101.46(2)
a_{B2}	—	3.08079(4)	3.08430(8)	3.08780(6)
$V_{B19'}$	—	58.524(8)	58.853(8)	58.79(1)
V_{B2}	—	29.241(1)	29.341(2)	29.441(2)

TABLE 3.4: Co-efficient of thermal expansion in the three crystallographic axes of B19' and B2 in $\text{Ni}_{35}\text{Ti}_{50}\text{Hf}_{15}$, $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ and $\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$, expressed in $\times 10^{-6}^\circ\text{C}^{-1}$

	$\text{Ni}_{35}\text{Ti}_{50}\text{Hf}_{15}$	$\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$	$\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$
$a_{\text{B19}'}$	10	13	20
$b_{\text{B19}'}$	-8	-13	-5
$c_{\text{B19}'}$	18	13	14
$\gamma_{\text{B19}'}$	-5	-16	-7
a_{B2}	9	11	11

both Hf and Zr are nearly the same [Slater, 1964; Pauling, 1947]. Surprisingly, the stoichiometric substitution of 3 at.% Cu for Ni on the Ni sublattice, which has a similar atomic radius to Ni [Slater, 1964], increases the B19' and B2 unit cell volumes, by 0.45% and 0.68% respectively.

The linear change in lattice parameter on heating and cooling away from the transformation regime is obviously interpreted as being due to thermal expansion. The negative change in $b_{\text{B19}'}$ with temperature can therefore be inferred to a negative thermal expansion in that direction. A negative thermal expansion coefficient in $b_{\text{B19}'}$ has also been observed in near equiatomic NiTi, refer Chapter 6. This is also evident from the negative changes with temperature in the $(11\bar{1})$, $(10\bar{1})$ and $(20\bar{1})$ interplanar distances reported by Qiu et al. [2009], indicating of negative thermal expansion coefficient along $c_{\text{B19}'}$ (or $b_{\text{B19}'}$ in a γ monoclinic angle setting). The thermal expansion coefficient in the three crystallographic axes of B19' and the B2 lattice parameter in all three HTSMAs in this investigation are listed in Table 3.4.

Large dilations and constrictions in the Rietveld-refined lattice parameters are observed in both the $\text{Ni}_{35}\text{Ti}_{50}\text{Hf}_{15}$ and $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ alloys during transformation, Figure 3.4, for example the $c_{\text{B19}'}$ of $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$ in 5th thermal cycle undergoes $\approx 0.2\%$ compression (less the thermal expansion) in the 5th thermal cycle between 200 and 230°C. The $a_{\text{B19}'}$ undergoes a 0.016 Å dilation in the same temperature regime and the monoclinic angle increases by in excess of 0.3° but no such abrupt changes appear obvious in case of $b_{\text{B19}'}$. On the contrary, large variations in $b_{\text{B19}'}$ in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ are observed during final stages of transformation. During heating, initially the B2 lattice in both alloys undergoes a contraction followed by a narrow temperature regime where it remains unchanged and then eventually undergoes a steep dilation during the final stages of transformation. The gradient da_{B2}/dT in final stages of transformation reduces with each thermal cycle (particularly in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$) and the sequence of events are exactly reversed during cooling in each cycle. The magnitude of change in the $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ B2 lattice is relatively very large compared to that in $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$. The role of transformation stresses due to the texture-related production / dissolution of habit plane variants of the martensite has been examined by selective examination of the diffraction patterns from different ring segments,

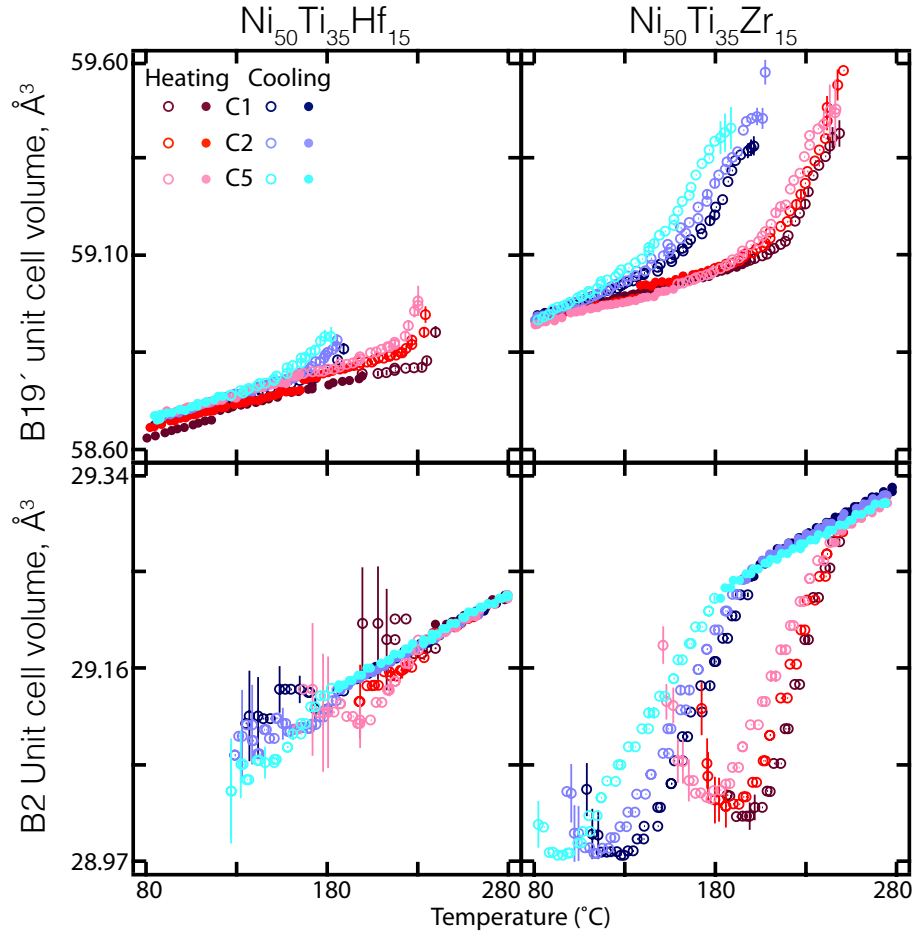


FIGURE 3.5: B2 and B19' unit cell volume evolution in $Ni_{50}Ti_{35}Hf_{15}$ and $Ni_{50}Ti_{35}Zr_{15}$. Solid symbols are in single phase region and open symbols during transformation.

and the dilations were unchanged. This suggests that residual stresses were not the primary cause of this behaviour. This issue is examined in more detail in Chapter 6.3

At the end of each thermal cycle, the B19' lattice parameters undergo a permanent shift. For example, the initial room temperature $b_{B19'}$ lattice parameter in $Ni_{50}Ti_{35}Zr_{15}$ was $4.8548 \text{ \AA}$ and after first thermal cycle the new $b_{B19'}$ room temperature lattice parameter was $4.8515 \text{ \AA}$, a decrease of $0.003 \text{ \AA}$. The shift however reduces in subsequent cycles. On the contrary, the B2 lattice in both alloys does not show such stepped evolution and away from transformation regime the a_{B2} at a given temperature in each cycle is always same.

This finding can be rationalised by appealing to the evolution of the defect state in the materials; for instance an evolution in B2 peak width with cycling was observed which, at least in NiTi, appears to be due to the production of dislocations [Simon et al., 2010; Jones and Dye, 2011]. In the B19', these dislocations therefore result in an evolution in the lattice parameters due to the relaxation of the interface stresses by dislocations.

The evolution of unit cell volumes of B2 and B19' in both alloys with temperature are provided in Figure 3.5. Away from transformation, the B19' unit cell volume in $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$ and $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ increases at a rate of 1×10^{-3} and $0.9 \times 10^{-3} \text{ \AA}^3 \text{C}^{-1}$ respectively. During the transformation, the change in unit cell volume for one phase appears to be complemented by a similar change in the the other.

The evolution of the B2 and B19' lattice parameters in $\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$ are shown in Figure 3.6. As in the other two alloys, the coefficients of thermal expansion here are positive for $a_{\text{B19'}}$ and $c_{\text{B19'}}$ and negative along $b_{\text{B19'}}$.

During transformation, the magnitude of dilation or contraction observed along each crystallographic axis are much smaller than the dilations in the other two alloys. For example, the maximum $a_{\text{B19'}}$ dilation in $\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$ during transformation is about 0.006, $\approx 0.7 \times$ larger than that observed in $\text{Ni}_{35}\text{Ti}_{50}\text{Hf}_{15}$. Unlike in the other two alloys, the $c_{\text{B19'}}$ and the B19' unit cell volume in $\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$ does not show large deviations from linearity. However, the changes in a_{B2} are far from linear within transformation regime. The B2 unit cell volume increases at a rate of $0.001 \text{ \AA}^3 \text{C}^{-1}$, similar to that of $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$, and the B19' lattice undergoes a stepped transformation like in other two alloys. The maximum M_s temperature reported by Meng et al. [2010] in their investigation on $\text{Ni}_{44}\text{Ti}_{36}\text{Hf}_{15}\text{Cu}_5$ ribbon samples was $150 \text{ }^\circ\text{C}$ which is comparable to the M_s for $\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$ observed in the current investigation.

Figure 3.7 shows the macroscopic dilations in all three alloys during thermal cycling along the tensile axis recorded using the ETMT cross head displacement. Since resistance heating produces a parabolic temperature profile across the sample, these changes cannot be directly related to the macroscopic strains experienced in the diffraction gauge volume at a specific temperature, but they do provide a qualitative indication of the macroscopic dilation hysteresis.

The macroscopic linear displacement at transformation temperatures away from the transformation regime corresponds to the thermal dilation (on heating) or contraction (on cooling) of the B19' and B2 phases. The dilation during transformation is a resultant effect of both linear thermal change and the transformation volume change modified by the overall variant relationships, which are dependent on the texture of the sample. The displacements in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ are an order of magnitude smaller than those observed in the other two alloys due to the fact that a much smaller gauge length specimen was used in that experiment.

The residual displacements at the end of each thermal cycle observed macroscopically in Figure 3.7 are presumably a reflection of the evolution in the B19' lattice parameters between thermal cycles observed in Figures 3.4-3.6. Clearly, the thermal hysteresis is smallest in $\text{Ni}_{47}\text{Ti}_{35}\text{Hf}_{15}\text{Cu}_3$ and largest in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$. This suggest that Cu additions are desirable for actuator applications. However, a corollary is necessarily that a lack of displacement hysteresis

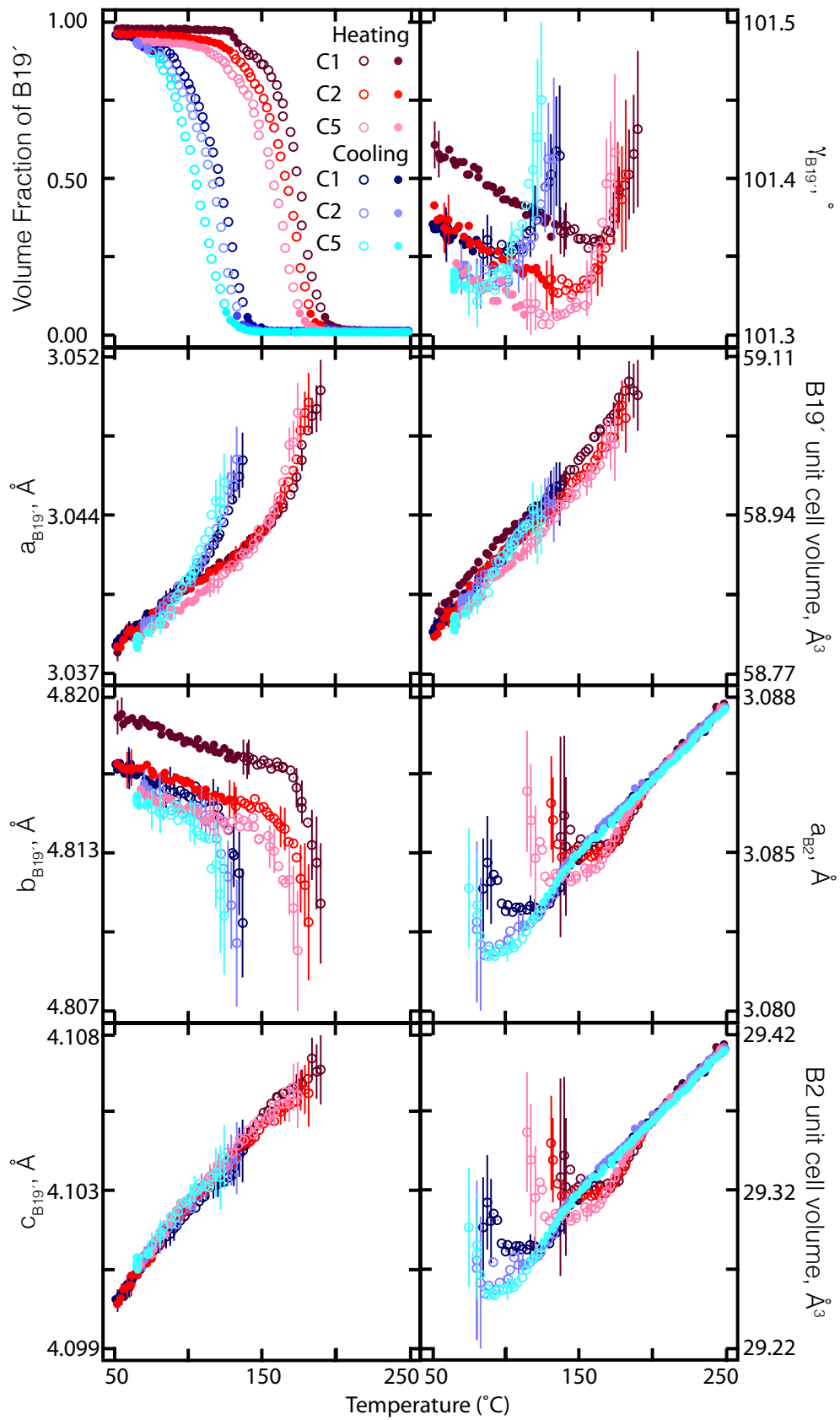


FIGURE 3.6: Lattice evolution in $Ni_{47}Ti_{35}Hf_{15}Cu_3$. Solid symbols are in the single phase region and open symbols during transformation.

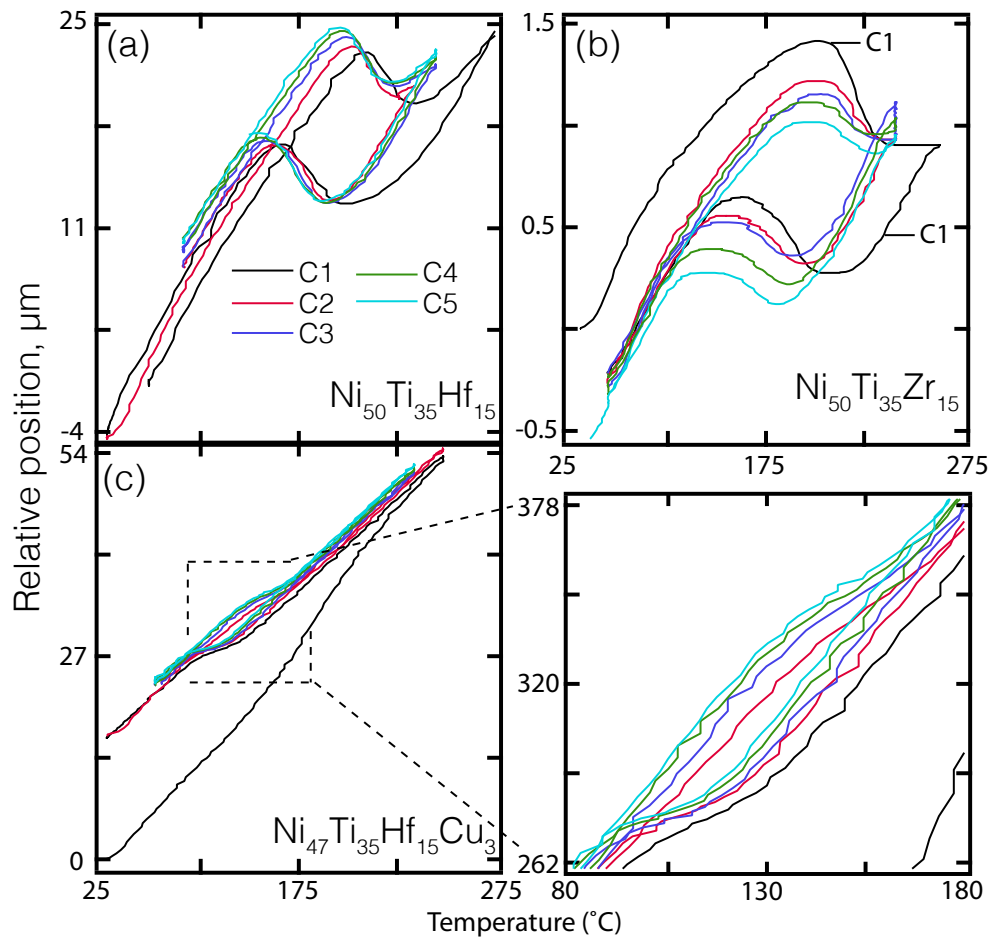


FIGURE 3.7: Dilatation in macroscopic specimens during thermal cycling in (a) $Ni_{50}Ti_{35}Hf_{15}$, (b) $Ni_{50}Ti_{35}Zr_{15}$ and (c) $Ni_{47}Ti_{35}Hf_{15}Cu_3$. A magnified version of transformation regime in (c) is provided in the bottom right section

in dilatometry does not necessarily indicate stability of the TTs on thermal cycling, so the size of the displacements measured using dilatometry cannot on its own be used to rationalise the temperature stability of SMAs.

At the end of the tests after five thermal cycles, each of the alloys were elastically loaded *in situ* in the B2 and B19' states to obtain the diffraction elastic constants (DECs) of the (020) and (002) B19' and the 110 of B2 for $Ni_{50}Ti_{35}Hf_{15}$ and $Ni_{47}Ti_{35}Hf_{15}Cu_3$. Ring segments in

TABLE 3.5: Diffraction elastic constants in GPa along (020) and (002) of B19' and (110) of B2 in $Ni_{35}Ti_{50}Hf_{15}$ and $Ni_{47}Ti_{35}Hf_{15}Cu_3$. DECs for $Ni_{49.8}Ti_{50.2}$ from Jones and Dye [2011] are provided for comparison

	$Ni_{49.8}Ti_{50.2}$	$Ni_{35}Ti_{50}Hf_{15}$	$Ni_{47}Ti_{35}Hf_{15}Cu_3$
$E_{B19'(010)}$	156	104 ± 3	108 ± 6
$E_{B19'(001)}$	203	82 ± 2	91 ± 3
$E_{B2(110)}$	—	76 ± 1	79 ± 2

the longitudinal direction between 80 and 100° were used to measure the changes in lattice parameter along the straining direction. The diffraction elastic constant is the relative change in lattice parameter per unit stress; it is a grain environment-modified measure of the single crystal elastic constants $C(ij)$, but extraction of these requires additional modelling effort and involves a number of micromechanical assumptions [Wagner and Windl, 2008]. The measured DEC's are provided in Table 3.5, along with the stiffness of identical directions in equiatomic NiTi taken from Jones and Dye [2011] for comparison. The brittle Ni₅₀Ti₃₅Zr₁₅ alloy failed early on during loading in the B19' state and therefore DEC's for that particular alloy could not be measured.

Clearly, the B19' in HTSMAs is less stiff than that in equiatomic NiTi. Alloying also seems to affect the elastic anisotropy, in NiTi while the $E_{B19'(010)}$ is smaller than the $E_{B19'(001)}$, reverse is observed in the HTSMAs. The Ni₃₅Ti₅₀Hf₁₅ lattice appears to be slightly more compliant than Ni₄₇Ti₃₅Hf₁₅Cu₃. This seems to have a significant impact on the peri-transformation evolution of b_{B19} and c_{B19} parameters. For example, during transformation in Ni₃₅Ti₅₀Hf₁₅ large constriction are observed in the $c_{B19'}$ and no deviation from initial linearity is observed in $b_{B19'}$, the behaviour is reversed in Ni₄₇Ti₃₅Hf₁₅Cu₃ and c_{B19} in this alloy undergoes a large contraction during transformation.

3.4 Conclusions

The behaviour of hot rolled polycrystalline NiTi alloys containing 15 at.% Hf and Zr have been examined using synchrotron X-ray diffraction and the effect of a 3 at.% Cu addition studied. The following conclusions can be drawn from the work in this Chapter.

1. Relatively low cost Hf and Zr-containing NiTi HTSMAs can be produced with transformation temperatures significantly higher than those of conventional NiTi SMAs. However, the thermal hysteresis $A_f - M_f$ of the alloys examined here is quite large, in excess of 70°C and the functional degradation per cycle is also relatively high and therefore these alloys are not yet practical actuator materials.
2. 3 at.% Cu additions did not significantly reduce the cyclic degradation of the transformation temperatures but did result in significant reductions ($> 50^\circ\text{C}$) in the transformation temperatures. However, the macroscopic dilations observed in the Cu-containing alloy were relatively small.

3. Invariably, a small fraction of $(\text{Ti,X})_2\text{Ni}$ was observed in the alloys fabricated, but fewer of these were found in the -Hf containing alloys than the -Zr alloys. The $\text{Ni}_{35}\text{Ti}_{50}\text{Zr}_{15}$ alloy was found to be brittle.
4. A per-cycle evolution in the B19' lattice parameters and unit cell volume was observed, but no such evolution was observed for the B2 phase. It is suggested that this may be due to the accumulation of interface dislocations.
5. For the first time peri-transformation lattice evolution in participating phases has been captured in great detail. Large dilations and constrictions in both martensite and austenite lattices are observed in all alloys, particularly in final stages of transformation. The additions of 3 at.% Cu at the expense of Ni in $\text{Ni}_{35}\text{Ti}_{50}\text{Hf}_{15}$ seems to have a large impact on the evolution of lattices, although it does not appear to significantly alter the lattice stiffness.
6. The diffraction elastic constants $E_{\text{B19}'(010)}$ and $E_{\text{B19}'(001)}$ in all alloys in the current investigation were relatively much smaller than those observed in equiatomic NiTi.

Chapter 4

Zr₅₀Cu₂₅Co_{12.5}Ni_{12.5} High Temperature Shape Memory Alloy

Summary

The transformation behaviour on thermal cycling of polycrystalline Zr₅₀Cu₂₅Co_{12.5}Ni_{12.5} high temperature shape memory alloy was examined by in situ synchrotron X-ray diffraction. The martensite finish temperature was found to be 294°C but the hysteresis was around 161 °C. The thermal expansion of both phases was found to be quite large, $33 \times 10^{-6} \text{ K}^{-1}$ in the B2 and $29 - 88 \times 10^{-6}$ for $a_{B19'}$ – $c_{B19'}$. Large deviations in the B19' lattice parameters, up to 2%, were observed during the transformation and particularly on heating. In contrast, the B2 lattice parameters remained undisturbed. The possible mechanisms behind these deviations are discussed.

4.1 Introduction

Intermetallic shape memory alloys such as NiTi and Ni₂MnGa deform *via* a diffusionless transformation from one crystal structure to another on changes in temperature, stress state and, in some alloys, under the influence of magnetic field. Usually, the high temperature (austenite) phase has high symmetry and this shears on transformation into twin-related variants of the product low symmetry, low temperature (martensite) phase. On loading of martensitic shape memory alloys (SMAs) a stress plateau is usually observed associated with detwinning of the martensite. In contrast, the phase transformation that occurs during zero stress thermal cycling results in the production of twin-related variant assemblies in each parent austenite grain. The

presence of a bias stress during thermal cycling allows a degree of variant selection to occur, a phenomenon that may also be induced by the presence of nucleating intermetallics or by cold working to engineer the grain boundary and defect state. Typically, the transformation proceeds gradually and a hysteresis is observed which is attributed to the energy dissipated in moving the austenite/martensite interfaces [Zarnetta et al., 2007; Delville et al., 2010; Zarnetta et al., 2010] which is in turn related to the availability of variants, self accommodation [Madangopal, 1997] and the interface strains that require the generation of interface defects [Pond et al., 2003].

SMA's are used or suggested for a wide variety of applications that each exploit different features of the behaviour. Austenitic seismic dampers [Dolce and Cardone, 2001] use transformation in each load cycle, making use of the large recoverable strain and hysteresis. In contrast, martensitic shape memory materials detwin the martensite at low temperatures and then recover the shape on heating; this is the phenomenon used in arterial stents [Duerig et al., 1999]. NiTi wires have been posited to actuate bistable air flow structures such as doors and air inlets in aircraft using thermal actuation. Recently, bimetallic NiTi / Ti thermal actuators have been suggested for noise control in gas turbine variable area nozzles [Birch and Webster, 2006; Calkins et al., 2006; Hartl and Lagoudas, 2007]. This leads to the suggestion that high temperature shape memory alloys (HTSMA's) could be used for airflow control elsewhere in gas turbines [Webster, 2006]. However, having a detailed understanding of the micromechanics of the transformations become more critical as multi-cycle, structural and more safety-critical components are suggested.

Most HTSMA's are ternary or quaternary alloys based on binary alloy systems. For example, NiTi based HTSMA's can be designed by stoichiometric replacement of Ti by Zr and Hf [Mulder, 1995; Van Humbeeck, 1999a; Firstov et al., 2004] or replacement of Ni by Pd [Huisman-Kleinherenbrink, 1991; Delville et al., 2009, 2010], Pt [Huisman-Kleinherenbrink, 1991] or Au [Huisman-Kleinherenbrink, 1991]. The transformation temperatures of the resulting alloys depend on the element(s) used and the extent of alloying. Apart from transformation temperatures SMA's may therefore be further classified based on the solubility limit of alloying elements, for example, in case of NiTi based alloys Pd could completely replace Ni and form a very high temperature equiatomic PdTi alloy while only a maximum of ≈ 20 at.% Ti can be replaced by Hf, Zr or Hf+Zr. The transformation temperatures of the NiTi based HTSMA's range from 100 to 900 °C but only a maximum of ≈ 300 °C has been achieved by using the low density and low cost alloying elements Zr and Hf.

ZrCu based HTSMA's seem to offer more desirable options than the NiTi based alloys in terms of the maximum transformation temperature and the economical ternary and quaternary alloying possibilities. The transformation temperatures of $Zr_{50}Cu_{25}Co_{25-x}Ni_x$ alloys increase with Ni content, with the maximum transformation temperature of ≈ 750 °C achieved in the

end-member $Zr_{50}Cu_{25}Ni_{25}$ alloy [Firstov et al., 1997]. In contrast, $Zr_{50}Cu_{25}Co_{25}$ undergoes transformation in the vicinity of room temperature. However, both equiatomic binary $ZrCu$ and $Zr_{50}Cu_{25}Co_{25}$ are reported to be brittle and the addition of Ni is observed to improve the ductility [Koval et al., 1994]. Increasing Ni beyond ≈ 15 at.% stabilizes a further martensite phase with the centered monoclinic (Cm space group) crystal structure instead of the conventional B19' martensite [Firstov et al., 1997]. The Cm phase in Zr intermetallics was first reported in binary $ZrCu$ [Firstov et al., 1997; Seo and Schryvers, 1997] and is always observed to be present to some extent in $ZrCu$ based alloys.

For efficient and reliable actuator design it is essential to have minimum evolution in properties such as the transformation temperatures during service. In SMAs the functionality depends on variant selection *vis-à-vis* self accommodation [Madangopal, 1997], interface energy [Delville et al., 2010] and the defect concentration, which are interdependent and related to the local stress states within grains in different orientations and to the material history. For example, the interface stresses depend on the difference in moduli of the participating phases and the overall defect concentration depends on many factors including the dislocation adsorption into growing twin boundaries. Crystallographic variants for a given set of phase candidates in a martensitic transformation can be predicted by using the phenomenological theory of martensitic transformations (PTMT) [Lieberman et al., 1955]. In tandem with a combinatorial search approach using thin strips, this has been used to identify stable NiTiCu alloys with minimum thermal hysteresis [Cui et al., 2006].

SMAs are commonly characterised using thermodynamic techniques in the bulk, such as calorimetry, dilatometry and resistivity, which do not reveal the evolution of crystallography-specific information; this limits the insight into the material evolution that can be obtained. Transmission electron microscopy (TEM) experiments can be used to gain such information but it cannot be directly correlated to the bulk behaviour because of the lack of constrain in thin films – for example, the transformation temperatures are sometimes found to be quite different.

In the present work, we use *in situ* synchrotron X-ray diffraction (sXRD) to examine the evolution of a $Zr_{50}Cu_{25}Co_{12.5}Ni_{12.5}$ alloy prepared by arc melting and hot rolling. This approach allows crystallographic information to be obtained whilst retaining the correct stress states representative of real actuators. It is found that this alloy does qualify as a high temperature shape memory alloy, with an austenite finish temperature (A_f) above 570 °C, but has high thermal hysteresis. Surprisingly, this is accompanied by relatively small per-cycle evolution in the transformation temperatures compared to NiTi-based HTSMAs [Kockar et al., 2006].

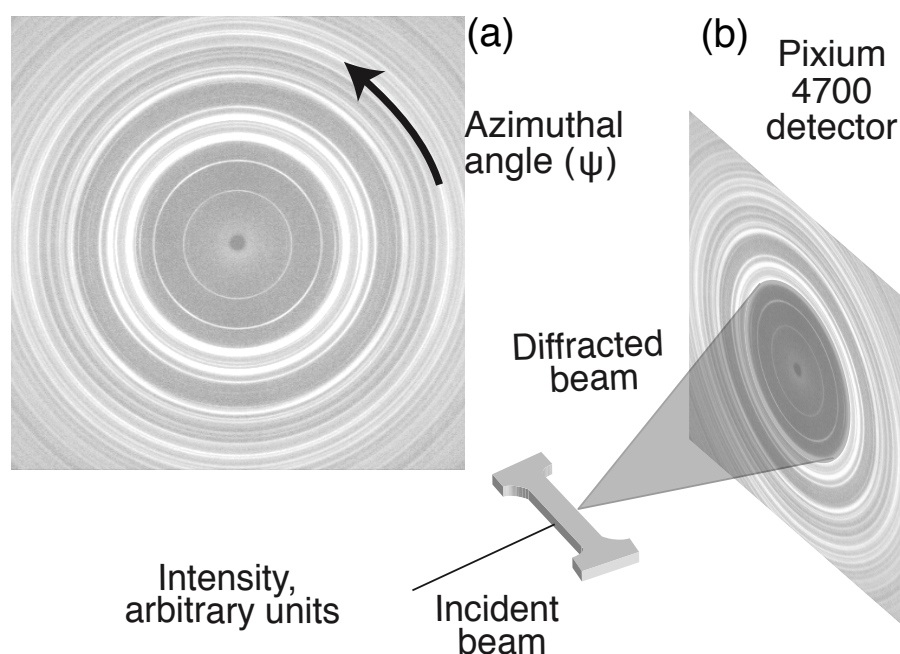


FIGURE 4.1: (a) Complete Debye-Scherrer rings from monoclinic martensite and (b) Schematic of the synchrotron X-ray diffraction setup

4.2 Experimental

The alloy was prepared by vacuum arc melting pure elemental Zr, Cu, Co and Ni in a pressure controlled pure Ar environment. The elements used were in lump form with a maximum dimension below 5 mm and very fine particles were avoided to eliminate elemental loss due to arc force during melting. A ~ 60 g ingot was prepared by melting and remelting with intermittent flipping to minimise elemental segregation. The ingot was encapsulated in quartz tubes and homogenised at 800 °C for 24 h, re-encapsulated in a steel can with commercially pure Ti powder to provide the necessary cushioning effect to minimise cracking and then hot rolled to 80% strain at 800 °C with 5 min interpass annealing. Sufficient plastic deformation from a process like rolling is necessary to produce recrystallisation in order to produce a fine enough grain size to observe complete Debye-Scherrer rings in diffraction, Figure 4.1a. Initial estimates of the transformation temperatures were obtained by calorimetry using a Mettler Toledo 822^e DSC. Flat dog-bone specimens with a $0.5 \times 0.5 \times 30$ mm gauge length were fabricated by electro-discharge machining and grinding. The specimen was then thermally cycled at a rate of 2 °Cs⁻¹ with a constant load of 5 MPa using an Instron electro-thermo mechanical testing machine (ETMT) at the ID15B powder diffraction beamline at the ESRF, Grenoble, France. A monochromatic beam of 0.5×0.5 mm with a wavelength of 0.1427 Å was used and the complete Debye-Scherrer rings recorded using a Thales Pixium 4700 detector [Daniels and Drakopoulos, 2009] mounted

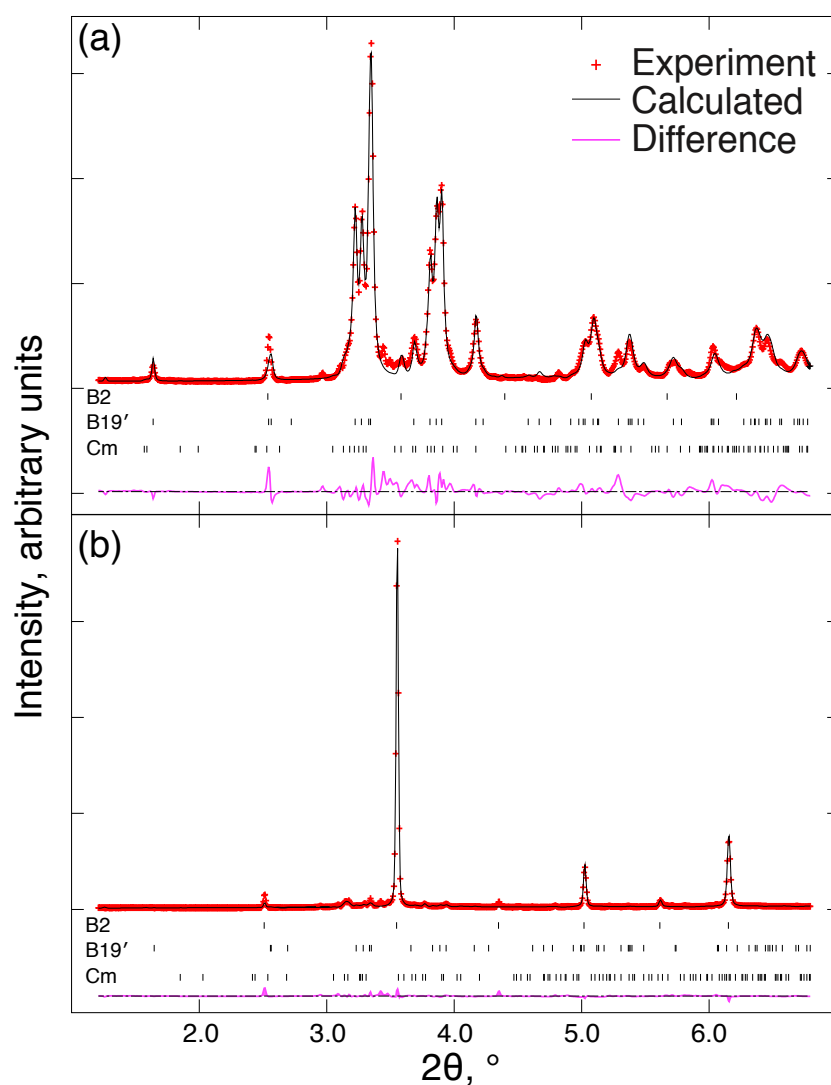


FIGURE 4.2: Diffraction spectra obtained from full-ring integration of 2D area detector data obtained during monochromatic high energy transmission X-ray diffraction of $Zr_{50}Cu_{25}Co_{12.5}Ni_{12.5}$ (a) in the low temperature monoclinic martensite state and (b) in the high temperature cubic austenite state. In both cases, during the first heat-up, a small amount of the CM phase is observed.

at a distance of 1.228 m from the sample, Figure 4.1b. The instrument parameters were determined using a LaB_6 calibration powder in a glass capillary. The temperature of the specimen was measured by an R-type thermocouple placed immediately above the diffracting volume. The position of thermocouple also facilitated in identifying the central gauge volume to a precision of 0.1 mm. This was necessary in order for the maxima in temperature produced by the quadratic temperature profile along the gauge length from resistance heating using water-cooled grips to be placed at the control thermocouple location. Rietveld refinement [Rietveld, 1969] of the whole-ring diffraction patterns, Figure 4.2a and 4.2b was used to obtain the phase fraction and lattice parameters, using the generalised structural analysis package (GSAS) [Toby, 2001;

Larson and Von Dreele, 1994] and the area detector analysis package Fit2D [Hammersley et al., 1996] – rephrase this.

4.3 Results

As an initial exploration of this candidate HTSMA system we focus on the behaviour of a single alloy which offers conventional B2 (austenite) $\leftrightarrow$ B19' transformation behaviour (low Ni content) but avoiding the intrinsic brittleness of Zr_2CuCo , in the anticipation that should this system prove promising then hysteresis minimisation will be possible using the PTMT approach to minimise the interface strains based on lattice parameter matching and Vegard's Law [Vegard, 1921]. Fine grained polycrystalline materials were arc-melted and hot rolled to refine the grain size. The alloy was found to be ductile in the martensitic state. The zero stress thermal transformation behaviour was studied using sXRD. The diffraction patterns obtained from the initial sample at room temperature (martensitic) and when first heated into the austenite phase are shown in Figure 4.2. The crystal parameters and phase fractions were then estimated using Rietveld refinement [Rietveld, 1969], using a spherical harmonic texture model [Sitepu et al., 2002] to account for the rolling texture of the sample.

The evolution of the diffraction patterns on thermal cycling in the region around the $\{110\}$ B2 peak is shown in Figure 4.3. The transformation from $P2_1/m$ B19' to $Pm\bar{3}m$ B2 first begins at around 475 °C and completes at around 570 °C. In the high temperature state, it is clear that a small amount of Cm phase remains, possibly accompanied by another intermetallic phase. On cooling, the (111) and (002) B19' peaks broaden and merge. For long term cyclic stability it is desirable for an SMA to undergo complete transformation from one phase to another but in reality a small amount of low temperature martensite remains untransformed in the microstructure on heating above the austenite finish temperature (A_f) [Basu et al., 2012] and *vice-versa* on cooling below martensite finish temperature (M_f) [Delville et al., 2009, 2010]. This presence of retained austenite in between growing martensite variant groups is expected to be due to the stress stabilisation of the austenite by the transformation strains [Delville et al., 2010]. In the current alloy the amount of retained martensite is slightly higher than that observed in the Zr- and Hf- containing NiTi based HTSMAs, refer Chapter 3.

Although the M_f temperature in the current alloy is very high, the overall transformation occurs over a wider temperature range (Figure 4.4) than the more commonly known NiTi based HTSMAs Meng et al. [2002], also refer Table 3.2 and Figure 3.4. The peak transformation temperatures, A_p and M_p ; corresponding to 50% martensite on heating and cooling are observed to be 498 and 337 °C respectively. Therefore the peak transformation hysteresis ($A_p - M_p$) in the

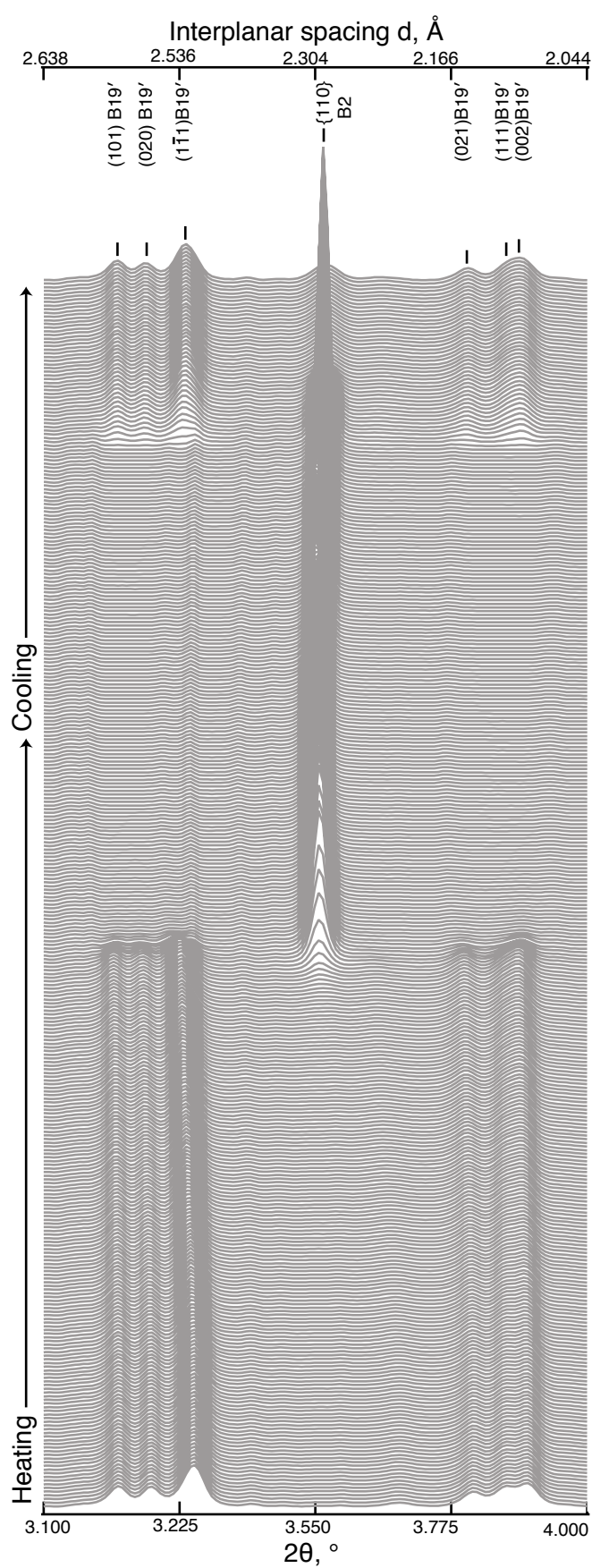


FIGURE 4.3: Evolution of a section of diffraction pattern during the first thermal cycle in $Zr_{50}Cu_{25}Co_{12.5}Ni_{12.5}$

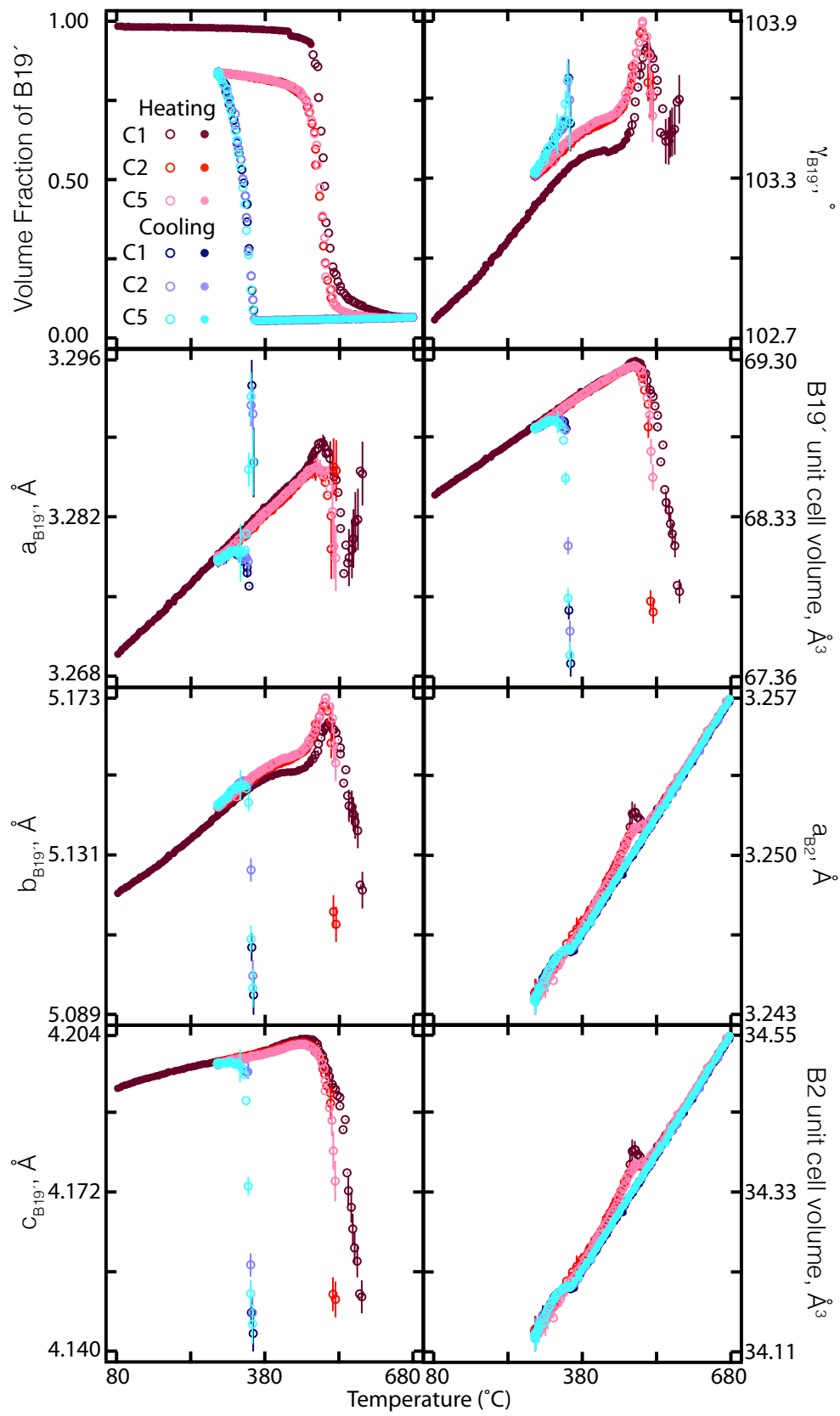


FIGURE 4.4: Monoclinic martensite and cubic austenite unit cell evolution evaluated as a function of specimen temperature. Solid symbols are in single phase region and open symbols during transformation. ‘V’ is the unit cell volume and subscripts t and c stands for tetragonal and cubic respectively.

TABLE 4.1: Transformation temperatures for all five thermal cycles (C1–C5) in °C. 80% volume fraction martensite was used as cut off limit for A_s and M_f and 10% was used for A_f and M_s .

	C1	C2	C3	C4	C5
A_s	488	421	420	420	419
A_f	576	523	522	525	522
M_s	357	355	354	354	355
M_f	296	295	295	294	294

current alloy is 161 °C, about 3.5 to 6× larger than in NiTi [Zarnetta et al., 2010] and $\approx 2.7\times$ larger than in the $Ni_{50}Ti_{35}Hf_{15}$ [Meng et al., 2002]. The forward B19' to B2 transformation occurs over a wider temperature range than the reverse transformation during cooling. For example, the transition from 80 to 10 % martensite during heating in cycle 5 occurs over 96 °C while on cooling this occurs over 58 °C. Further, the final dissolution from ≈ 20 to 5% martensite in each heating cycle occurs over a greater temperature range than re-occurrence at the beginning of a cooling ramp. The start and finish transformation temperatures are evaluated by applying a martensite volume fraction cut off limit of 80% for A_s and M_f and similarly a 10% limit is used for A_f and M_s ; the transformation temperatures for all five thermal cycles thus evaluated are listed in Table 4.1. A_s and A_f for the first heating cycle are ≈ 60 °C higher than the corresponding temperatures in the rest of the cycles, however, a similar difference was not observed for M_s and M_f .

Figure 4.4 also shows the evolution of the lattice parameters of the phases and the corresponding unit cell volumes in the alloy before inception and during the course of transformation in first, second and fifth thermal cycles. The lattice parameters of the B19' at room temperature and the B2 at 620 °C are provided in Table 4.2 along with the B2 and B19' phase parameters in binary near-equiatomic NiTi [Jones and Dye, 2011] and ZrCu [Schryvers et al., 1997]. Clearly, the B19' unit cell is larger than in NiTi and ZrCu and the B2 unit cell in current alloy is $\approx 0.4\%$ larger than in NiTi.

Because the monoclinic cell has two-fold centrosymmetry, thermal expansion can be uniquely described by the variation in a , b , c and γ , Table 4.2. Compared to conventional metals, both phases have quite high thermal expansion. In particular, $b_{B19'}$ is very large, at $88.2 \times 10^{-6} \text{ K}^{-1}$, and the monoclinic shear angle γ is heavily temperature dependent. This is probably best understood in terms of the high vibrational entropy (and soft phonons) of crystal structures associated with shear transformations.

Complete recovery is observed at the end of every thermal cycle in each of the B19' and B2 lattice parameters except the monoclinic angle γ which undergoes a permanent change of 0.11° (from 103.23° to 103.34° or 0.1%) on cooling at the end of the first thermal cycle, but subsequently

stabilises. In the investigation on NiTi based HTSMAs (Chapter 3) this evolution was observed over multiple monoclinic crystal parameters and cycles.

It is instructive to compare the B2 and B19' lattice parameters. $\sqrt{2}a_{B2} = 4.603 \text{ \AA}$ is nominally equivalent to $b_{B19'}$ and $c_{B19'}$, which in fact are around $\pm 10\%$ larger / smaller, which is similar in magnitude to the net shear of 12.7° . During the course of the heating transformation, very large decreases in the B19' lattice parameters are observed, Table 4.2 and Figure 4.4; for example, $a_{B19'}$ changes by -0.34% during the course of the transformation. These changes are not orientation-dependent; an analysis of different ring segments produces the same result. In $Ni_{50}Ti_{35}Hf_{15}$ alloy, the changes observed in the lattice along two orthogonal segments of the diffraction rings, Figure 6.3, were similar to the changes observed in the corresponding peaks in whole ring diffraction parameters, Figure 6.2. This suggests that the large changes in the lattice in vicinity of transformation are not the result of accommodation stresses. In the case of $a_{B19'}$ and $c_{B19'}$, these changes are away from the ideal B2 orientation relationship; that is, these are not gradual moves towards the B2 structure.

The reverse changes are observed on cooling, and at maximum, these strains are equivalent to a 2% dilatation. In addition, the transformation-associated changes in $a_{B19'}$ and $\gamma_{B19'}$ rise at the very end during heating. Finally, before transformation begins, $b_{B19'}$ and $\gamma_{B19'}$ undergo a cessation of thermal expansion, although it lasts over a small temperature range. However, this interruption is only confined to the heating transformation.

In complete contrast, no such large deviations are observed in the B2 phase on transformation.

TABLE 4.2: Coefficients of thermal expansion α_{th} , Rietveld refined lattice parameters of the B2 and B19' at 620°C and room temperature, along with the maximum transformation induced change (Δ) and the corresponding strain along the crystallographic axes of the two phases during transformation. Lattice parameters of B19' and B2 in NiTi [Jones and Dye, 2011] and ZrCu [Schryvers et al., 1997] are provided for comparison. Uncertainties for the current alloy are in parenthesis and for NiTi they are reported to be of the order of $\approx 10^{-3}$ [Jones and Dye, 2011]. Lengths are in $\text{\AA}$, B19' unit cell angle is in $^\circ$ and the unit cell volume is in $\text{\AA}^3$.

	ZrCu	$Zr_{50}Cu_{25}Co_{12.5}Ni_{12.5}$	NiTi	$\alpha_{th} \times 10^{-6} \text{ }^\circ\text{C}^{-1}$	$\Delta \text{ \AA, \AA}^3, ^\circ$	strain %
$a_{B19'}$	3.2	3.2688(6)	2.90	39.2(3)	-0.011	-0.34
$b_{B19'}$	5.2	5.1181(9)	4.65	88.2(9)	-0.044	-0.85
$c_{B19'}$	3.9	4.1913(7)	4.12	29.3(5)	-0.052	-1.25
$\gamma_{B19'}$	106	102.75(2)	97.5	1770(20)	-0.350	-0.34
a_{B2}	—	3.25489(7)	3.02	33.4(4)	-0.0005	-0.02
$V_{B19'}$	—	68.39(2)	—	—	-1.402	-2.05
V_{B2}	—	34.518(2)	—	—	-0.02	-0.05

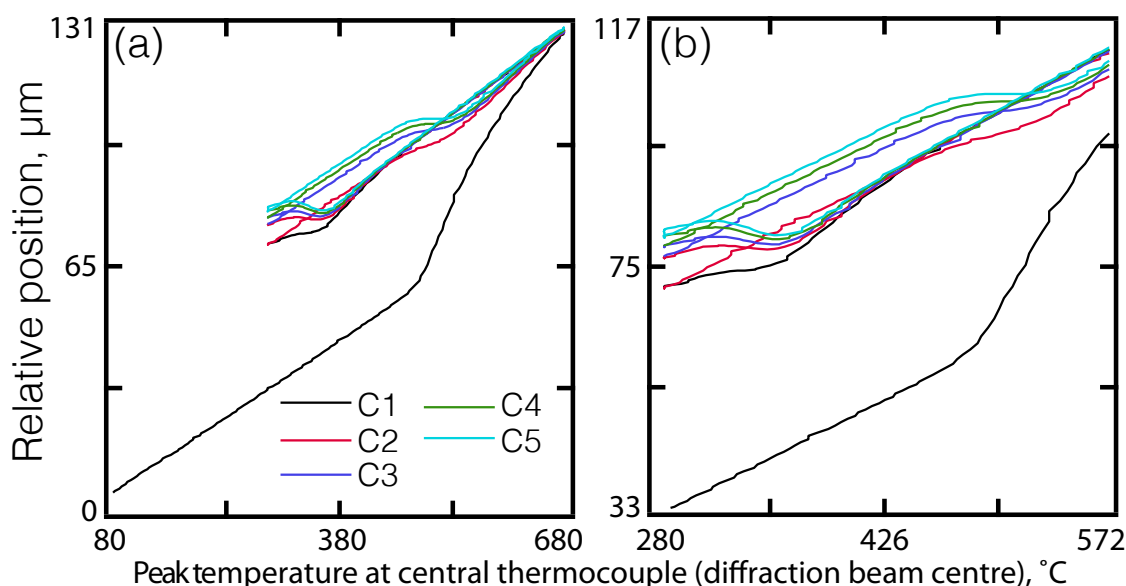


FIGURE 4.5: Overall actuator motion measured from the thermo-mechanical testing machine during transformation, (a) over the entire testing range and (b) in the vicinity of transformation.

Figure 4.5 shows the measured sample dilatations. Because resistance heating was used, which preferentially heats the central region where the diffraction beam and thermocouple were co-located, these cannot be directly converted to strain. However, they do indicate the macroscopic hysteresis observed in the sample and overall changes in specimen length at the ends of transformation. It is observed that the sample gradually extended over the five thermal cycles utilised, in common with most SMAs. In agreement with the diffraction results, they also indicate that A_f remained constant during cycles 2-5, but with a large change between cycles 1 and 2. In contrast, M_s and M_f remained fairly constant (again, consistent with the diffraction results), as did the actuator position at the end of the heating ramp.

4.4 Discussion

In the experiments performed here, the martensite transformation on cooling did not complete at the end of each thermal cycle; however on-heating austenite transformation did complete each time. The results are consistent with recovery of the same parent 100% austenite grain structure at the end of each heating and, after cycle 1. Therefore the lack of evolution in cycles 2-5 usually observed in SMAs possessing hysteresis is presumably due to the transformation not being run to complete dissolution of the austenite on cooling. However, that does not prevent the sample from gradually extending over the thermal cycling, which is most likely, from an examination of the diffraction patterns, to be due to a gradual variant selection process operating in the B19' phase.

The major challenge in interpreting the results observed here is understanding the lattice parameter changes that occur in the B19' on heating. Because the B19' – B2 interfaces are believed to be sharp [Delville et al., 2010] then for alloys where $\lambda_2 \neq 1$, *i.e.* with non-zero distortion on the interface plane (the present case), the large interface strains must be accommodated by interface defects. However, one can examine the present data against the following hypotheses - (i) that the changes are due to accommodation stresses between the laths and the B2, (ii) that they are a product of the defect configurations and martensite lath widths, (iii) that they are associated with physical changes in the crystal behaviours at the point of marginal stability. Zener pointed out that structures at the edge of stability must have low shear moduli in the shearing directions, and so the large strains observed might be consistent with a mechanical effect.

However, the lattice parameter changes are observed in different ring segments and as well as the entire-ring integrations presented here, which in the rolled sheet employed here would tend to suggest that the effect is not related to the specimen texture and therefore, to variant accommodation mechanisms. In addition, the volume change observed would mitigate against a variant accommodation stress mechanism, as would the lack of corresponding deviations in the B2. However, the inversion seen in the change in a_{B2} and $\gamma_{B19'}$ also suggests that this is not a product of, for instance, a softening in the elastic constants in the vicinity of transformation.

The lattice parameter changes observed, if interpreted as strains, are quite large, on the order of 1%. The first martensite to appear would be heavily constrained by the surrounding B2 but as it grew could relax increasing amounts of stress by the growth of adjacent variants; this could plausibly generate strains on the order of 1%, which is similar in magnitude to the yield strain of detwinned martensite. This line of reasoning does not, however, explain the minima observed in a_{B2} and $\gamma_{B19'}$ on heating only, and orientation independence. However, this occurs towards the end of transformation, when the austenite ribs between the B19' laths become thick enough to link up and for any variant accommodation effects to therefore cease to apply. At this point, interface defect effects may become dominant.

It is interesting to interpret these issues in relation to the phenomenological theory of martensite transformations. The special case where the interface strain is zero, $\lambda_2 = 1$, has been shown to be a criterion that minimises hysteresis [Cui et al., 2006], and in this case no interface defects will be produced and the elastic strains associated with martensite precipitation will be zero. However, far from this condition, as in the present case, an elastic analysis inspired by this approach will fail as interface defects and any associated anisotropy and stress fields will need to be accounted for.

4.5 Conclusions

The transformation behaviour of polycrystalline $Zr_{50}Cu_{25}Co_{12.5}Ni_{12.5}$ has been examined using synchrotron X-ray diffraction. The following conclusions can be drawn

- The alloy is a plausible candidate high temperature shape memory alloy, with a stabilised martensite finish temperature of 294 °C, but has a high hysteresis of around 161 °C.
- The alloy can be produced in a polycrystalline form and was found to be ductile.
- The thermal expansion coefficients were found to be quite large in both phases, $33 \times 10^{-6} \text{ K}^{-1}$ for the B2 and from $29\text{--}88 \times 10^{-6} \text{ K}^{-1}$ for $a_{B19'} - c_{B19'}$.
- Large deviations in the B19' lattice parameters, up to 2%, are observed during the transformation and particularly on heating. In contrast, the B2 lattice parameters remain undisturbed.

The mechanism of these deviations is not completely clear; however, the minima observed, the direction of the deviations away from the B2 ideal orientation relationship and the lack of mirroring deviations in the B2 all suggest that they cannot solely be due to elastic variant accommodation effects and that interface defects will also be a part of any complete explanation.

Chapter 5

Ni₅₄Mn₂₅Ga₂₁ Ferromagnetic High Temperature Shape Memory Alloy

Summary

Polycrystalline Ni₅₄Mn₂₅Ga₂₁ has been produced by conventional ingot metallurgy and hot working and examined as a thermal shape memory alloy using in situ synchrotron X-ray diffraction. It was found that M_f was 232 °C and A_f, 298 °C. A_f was observed to decline by 8 °C/cycle, which was attributed to the buildup of a population of defects. Both above and below the Curie temperature, the application of an e.m.f. was found to affect the lattice parameters measured. A change in the thermal expansion of the two phases was found around the Curie temperature.

5.1 Introduction

Ferromagnetic shape memory alloys (fSMAs) based on the Ni-Mn-Ga system [Chernenko et al., 1995] are of great interest both as actuators and as magnetocaloric materials. Posited examples range from fast actuation in aerodynamic control surfaces in aero-engines and structures [Hartl and Lagoudas, 2007; Birch and Webster, 2006] to a new generation of solid-state heat pumps that may offer a coefficient of performance (COP = Heat supplied or removed from the reservoir(Q)/Energy consumed by heat pump (W)) in excess of 4. Both of these applications will be of importance in the development of a low-carbon society. In addition to stress and temperature, the shape memory functionality in fSMAs is realised using an applied magnetic field, allowing for fast actuation. Large magnetic field induced strains (MFIS) are widely reported in these alloys [Kim et al., 2006; Sozinov et al., 2002; Chmielus et al., 2009; Jenkins et al., 2008;

[Jeong et al., 2003](#)] and the underlying mechanism is thought to be the magnetically induced mobility of twin interfaces [[Sozinov et al., 2002](#); [Murray et al., 2000](#)].

In the Ni-Mn-Ga system, shape memory effect was first observed in the Heusler compound Ni_2MnGa [[Webster et al., 1984](#)] and the ferromagnetic phase transformation was discovered almost a decade later in off-stoichiometric Ni-Mn-Ga alloys [[Xu et al., 2003](#)]. The TTs in this system are sensitive to deviations from the Heusler stoichiometry; variations of ~ 50 °C per at.% Ni substitution for Ga have been reported [[Chernenko et al., 1995](#); [Lanska et al., 2004](#); [Chernenko et al., 2002](#)] but surprisingly the change in composition has a very modest effect on the Curie temperature (T_c) [[Chernenko et al., 1995](#); [Lanska et al., 2004](#)]. It is reported that the TTs in this system increases linearly with increases in the electron to atom ratio (e/a) [[Chernenko et al., 2002](#); [Jiang et al., 2003](#); [Wu and Yang, 2003](#)]. Therefore, in developing high temperature Ni-Mn-Ga alloys, increase in Ni at the expense of Ga is generally preferred as Ni has the highest number of valence electrons and since the fraction of Ni in the alloy is the highest. For example, the M_f in a $Ni_{54}Mn_{24.7}Ga_{21.3}$ alloy ($e/a = 7.768$) [[Lanska et al., 2004](#)] is ~ 215 °C higher than near-stoichiometric $Ni_{50}Mn_{25}Ga_{25}$ ($e/a = 7.5$) [[Kim et al., 2006](#); [Wu and Yang, 2003](#); [Pons et al., 2000](#); [Brown et al., 2002](#)].

Irrespective of composition, the austenite in Ni-Mn-Ga alloys is reported to be $L2_1$ ($Fm\bar{3}m$ space group) but the martensite crystal structure varies considerably with small changes in composition [[Lanska et al., 2004](#); [Richard et al., 2006](#)]. Both modulated and non-modulated martensites have been reported; 5M and 7M modulated martensites are observed in alloys with Curie temperatures (T_c) higher than the TTs whilst non-modulated martensites are observed in alloys where T_c is lower than TTs [[Lanska et al., 2004](#)]. In Mn rich alloys with ~ 20 at.% Ga, orthorhombic and tetragonal martensites are observed, and for certain compositions both forms can co-exist [[Richard et al., 2006](#)]. It is observed for the tetragonal martensite that increases in e/a increases the amount of tetragonality, c_t/a_t [[Pons et al., 2000](#)].

Single crystals have been used in most investigations on Ni-Mn-Ga alloys, however, for ease of production and widespread functional-structural application it is desirable to implement alloys in polycrystalline form. In this context, purely thermal high temperature Ni_2MnGa actuators may also be of interest, although they would be slower-acting. Normally, SMAs show significant functional fatigue, with the TTs dropping with each cycle such that a practical actuator with a service life of thousands of cycles remains difficult to produce.

Here, we focus on the characterisation of the thermal transformation in polycrystalline off-stoichiometry $Ni_{54}Mn_{25}Ga_{21}$ by synchrotron X-ray diffraction, with an emphasis on the evolution of the unit cell parameters of the participating phases. This particular composition was chosen for two reasons (i) the transformation in this alloy is single step (cubic $\leftrightarrow$ tetragonal) [[Ma](#)

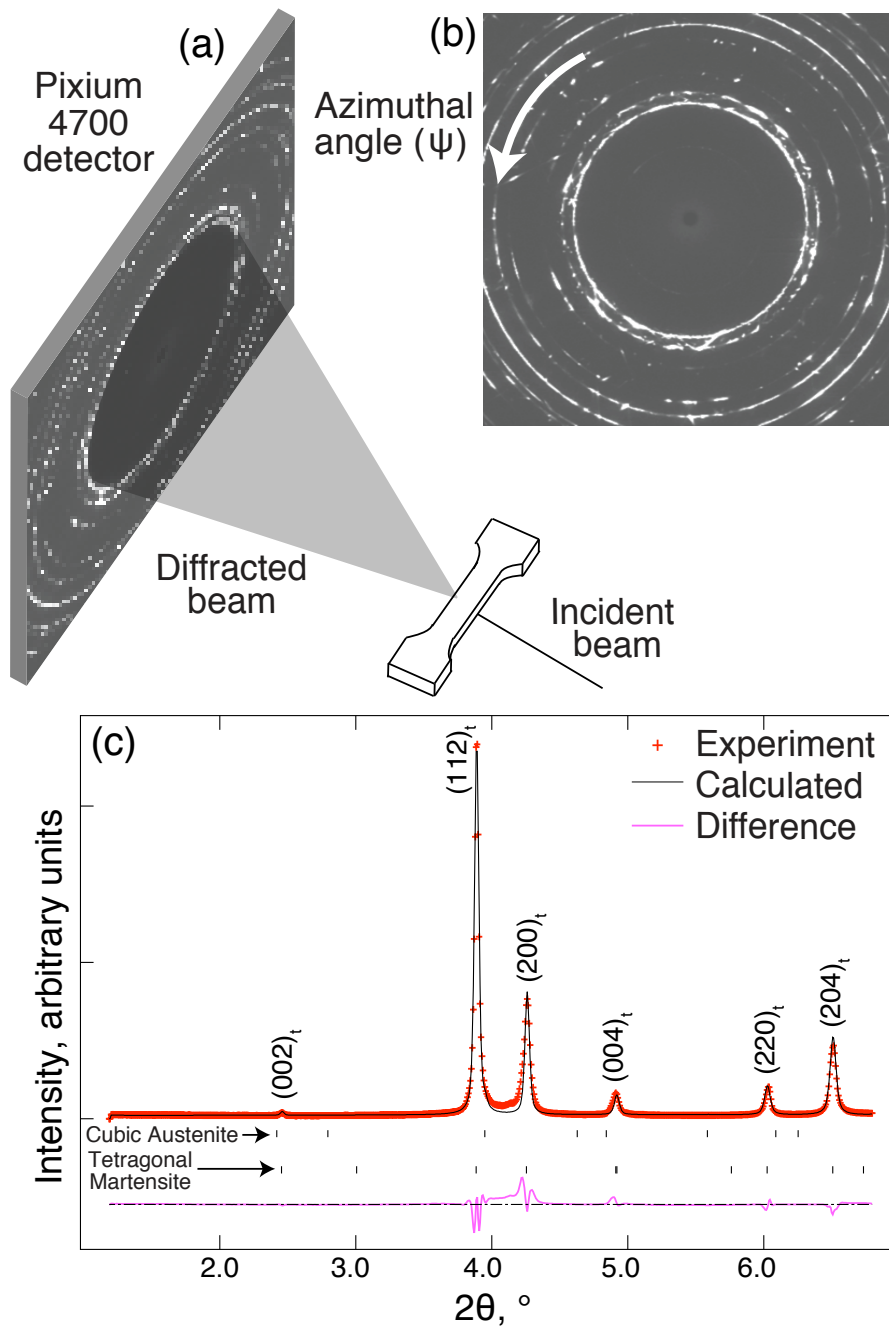


FIGURE 5.1: (a) Schematic of the synchrotron X-ray diffraction setup, (b) Complete Debye-Scherrer rings from tetragonal martensite and (c) Diffraction spectra after 360° intensity integration across diffraction rings in (b)

et al., 2003; Cong et al., 2005] and (ii) the alloy is a potential high temperature shape memory candidate with TTs in excess of 200°C [Ma et al., 2003].

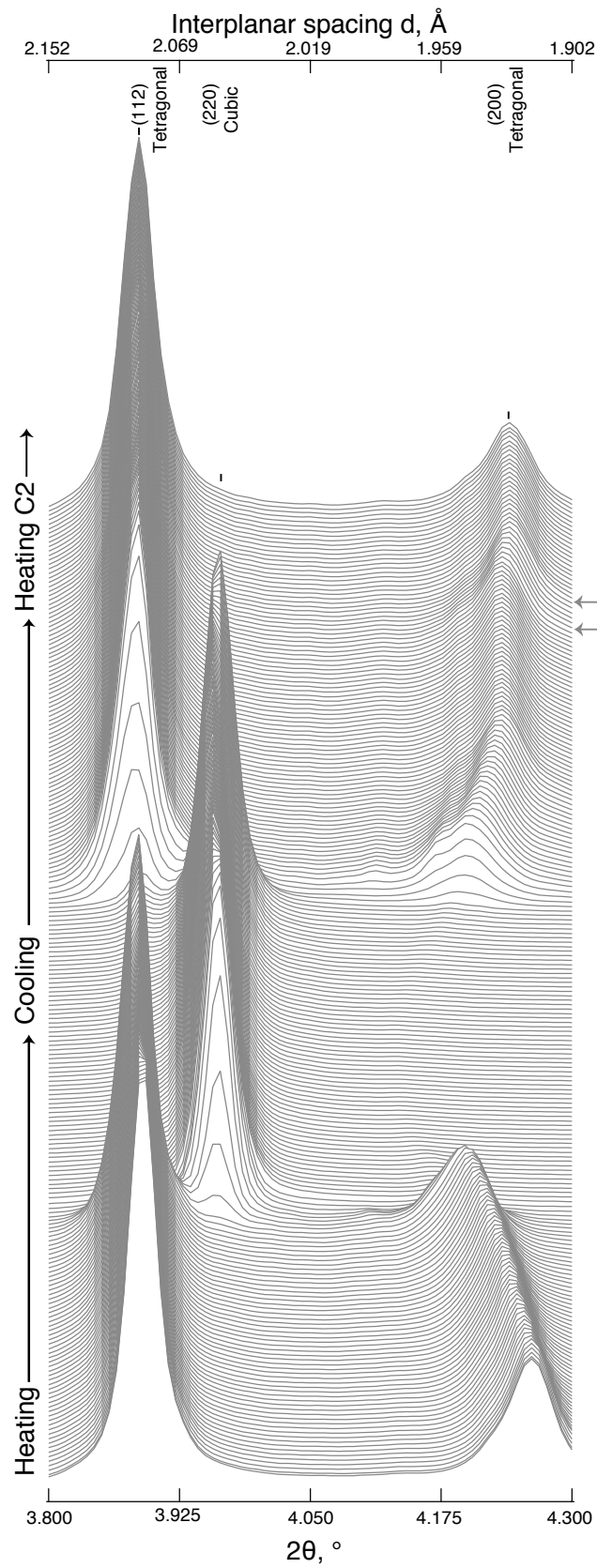


FIGURE 5.2: Evolution of a section of diffraction pattern during the first thermal cycle in $Ni_{54}Mn_{25}Ga_{21}$. The e.m.f reversal regime during which a shift in martensite lattice parameters was observed is indicated by arrows on the right.

5.2 Experimental

The alloy was prepared by vacuum arc melting pure elemental Ni, Mn and Ga in pure argon. The ingot was remelted 4-5 times and inter melt flipped to minimise elemental segregation. The evaporation of Ga due to the arc force during the first melt was minimised by uniformly distributing the other two elements above the Ga in the melt cavity. The ≈ 60 g ingot was encapsulated in a quartz tube and then homogenised at 900°C for 24 h. The ingot was then encapsulated in a mild steel can, stuffed with Ti powder for cushioning and then Hot rolling at 900°C with a 5 minute inter pass annealing at 900°C . $0.5 \times 0.5 \times 30$ mm gauge length specimens were then fabricated by grinding and electro-discharge machining (EDM). Differential scanning calorimetry using a Mettler Toledo DSC 822^e instrument was used to obtain initial estimates of the TTs. The specimen was then thermally cycled at a rate of 2°Cs^{-1} at zero load in an Instron 5 kN resistance heating electro-thermal mechanical testing machine (ETMT) at the ID15B powder diffraction beamline at the ESRF, Grenoble France, Figure 5.1a. A wavelength of $0.1427 \text{ \AA}$ was used and the incident beam was approx. 0.5×0.5 mm in size. A Thales Pixium 4700 detector [Daniels and Drakopoulos, 2009] was used to collect complete Debye-Scherrer diffraction rings (Figure 5.1b) at a sample-detector distance of 1.228 m. A LaB_6 calibration powder was used to determine the instrument parameters. Specimen temperatures were measured using an R-type thermocouple placed immediately above the diffracting volume, to a precision of 0.1 mm. Phase fractions and lattice parameters were obtained by Rietveld [1969] refinement of the whole-ring diffraction patterns, Figure 5.1c, ignoring orientation-specific strains due to, *e.g.* the rolling texture, using the generalized structural analysis package (GSAS) [Toby, 2001; Larson and Von Dreele, 1994] and the area detector analysis package FIT2D [Hammersley et al., 1996].

5.3 Results and Discussion

The high temperature (austenite) phase in $Ni_{54}Mn_{25}Ga_{21}$ has an $Fm\bar{3}m$ crystal structure with Ni at $(1/4, 1/4, 1/4)$, Mn at $(1/2, 1/2, 1/2)$ and Ga at $(0,0,0)$ and $a_c = 5.8468 \pm 0.0003$ at 320°C . In the absence of stress and magnetic field, the martensite was observed to be tetragonal with lattice parameters $a_t = 3.8391 \pm 0.0003$, $c_t = 6.650 \pm 0.001$ and $c_t/a_t = 1.732$. Comparing these with the lattice parameters for $Ni_{53}Mn_{25}Ga_{22}$ reported by Cong et al. [2005]; $a_t = 3.865$, $c_t = 6.596$ and $c_t/a_t = 1.707$, the increase in c/a achieved by increasing Ni (at the expense of Ga) in the current alloy appears to have changed the c/a ratio considerably. The main orientation relationship in $Ni_{53}Mn_{25}Ga_{22}$ is reported to be $(111)_c \parallel (101)_t$, $[110]_c \parallel [111]_t$ [Cong et al., 2007].

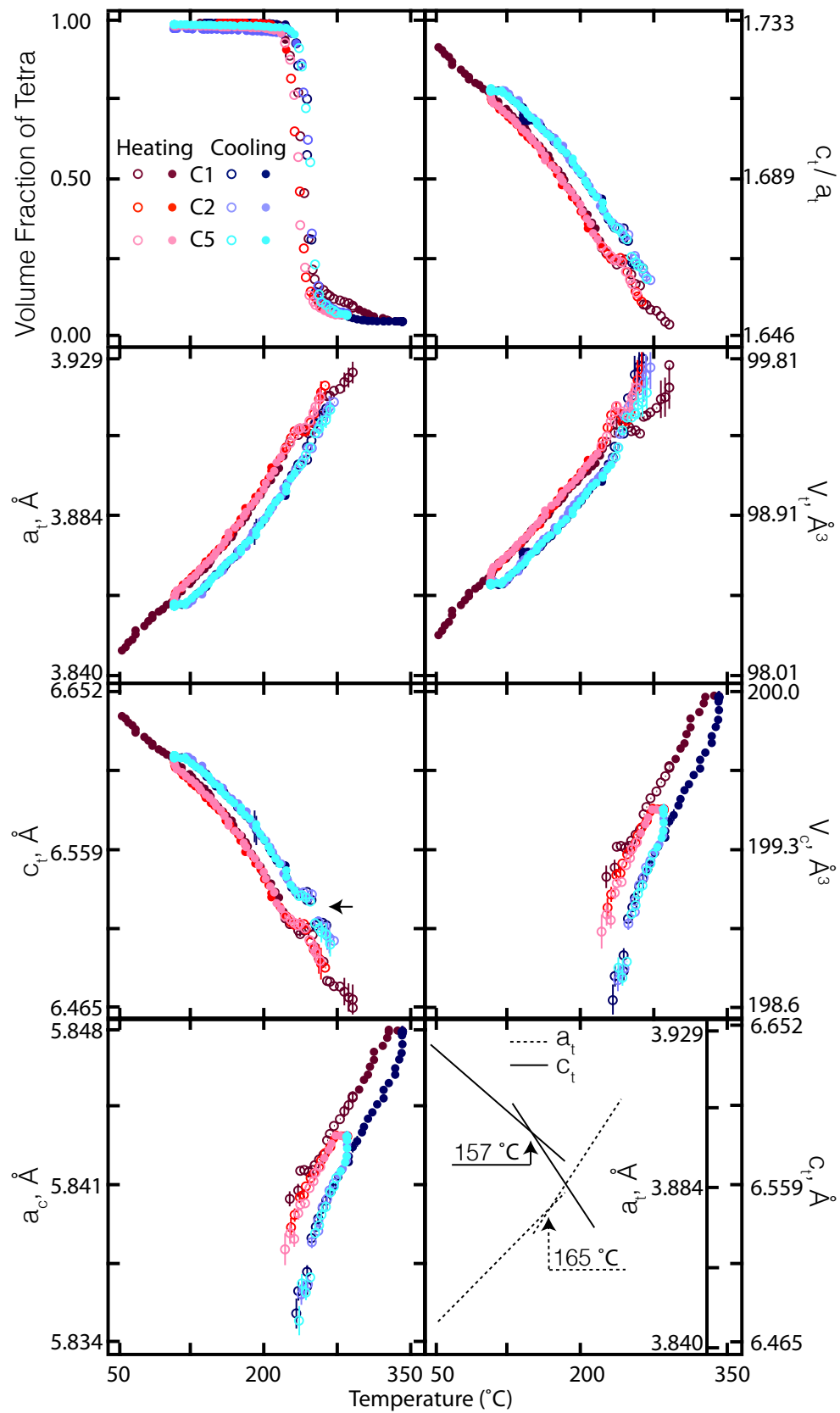


FIGURE 5.3: Tetragonal martensite and cubic austenite unit cell evolution evaluated as a function of sample temperature. Solid symbols are in single phase region and open symbols during transformation. 'V' is the unit cell volume and subscripts t and c stands for tetragonal and cubic respectively.

The transformation sequence in the first thermal cycle is shown in Figure 5.2. A large dilation in the $d_{(200)}$ interplanar spacing in the tetragonal martensite was clearly visible on heating and cooling. A new peak was observed in vicinity of the tetragonal (200) peak during very last stages of heating and during initial stages of cooling, but apart from this no additional peaks were observed elsewhere in the spectra. The extra peak disappears or merges with the (200) peak as the sample is heated or cooled. Due to presence of a lone peak it is difficult to confirm the presence of an intermediate phase. A subtle but yet visible shift in the (200) tetragonal peak is observed (arrowed) on final cooling and before reheating began, which is discussed later.

The sample was also loaded in tension after thermal cycling, it was found to be brittle with a strength of less than 100 MPa.

The Rietveld-refined lattice parameters and phase fractions are shown in Figure 5.3. The transformation from tetragonal to cubic after stabilization in cycle 1 first begins on heating at around 213°C with 80% of the cubic phase appearing over 227 – 258 °C, after which the transformation rate decreases with temperature before final completion at 286°C. The measurement points occur approximately every 5 °C, allowing the austenite and martensite start and finish temperatures (at 90% / 10% phase fraction) to be interpolated with an accuracy of around 3 °C, Table 5.1

The fitted lattice parameters, Figure 5.3, show almost no change between successive thermal cycles, which is a good indicator of thermal stability. For example, the change in a_t at 125 °C after four thermal cycles was only 0.04% (Table 5.1). The thermal expansion coefficients (α_{th}) of a_t and c_t are found to be $7.7 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ and $-6.9 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ respectively. At $\approx 160 \text{ }^\circ\text{C}$ (slightly above the expected Curie temperature [Lanska et al., 2004; Cong et al., 2005]), a visible

TABLE 5.1: Lattice parameters (Å) of tetragonal martensite on cooling and heating (at 125 °C for martensite and at 270 °C for austenite), where, c and h superscripts are for cooling and heating, A_s , A_f , M_s and M_f are austenite start, finish, martensite start and finish respectively.

	Cycle1	Cycle5
a_t^h	3.8653 ± 0.0003	3.8667 ± 0.0004
a_t^c	3.8606 ± 0.0004	3.8604 ± 0.0003
c_t^h	6.603 ± 0.001	6.600 ± 0.001
c_t^c	6.611 ± 0.001	6.612 ± 0.001
a_c^h	5.8433 ± 0.0003	5.8425 ± 0.0002
a_c^c	5.8403 ± 0.0003	5.8403 ± 0.0002
A_s	226	227
A_f	298	258
M_s	267	268
M_f	232	236

change in linearity is observed and the thermal expansion / contraction appears to accelerate; *i.e.*, the a_t now dilates and c_t constricts at a much faster rate than previously. These events are schematically highlighted in the final subfigure in Figure 5.3. The reverse behaviour is observed on cooling and the inflection point at which the α_{th} changes is now slightly higher than 160 °C. In the cubic high temperature phase, the corresponding thermal expansion coefficient is measured to be $1.3 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$. During transformation, contraction of c_t initially ceases (at $\approx 235 \text{ }^\circ\text{C}$), but during the final stages of transformation it resumes; a similar behaviour in reverse is observed for a_t . During cooling, at approximately 256 °C, indicated by arrow in Figure 5.3, there appears to be a rather large instantaneous jump in c_t . This change is not observed on heating, and is repeated in each thermal cycle.

Interestingly, a hysteresis is observed in the lattice parameters in both the cubic and tetragonal phases, not associated with the transformation, which collapses when the heating direction reverses; in the first thermal cycle (brown / dark blue) which reversed at 345°C the lattice parameters converge at that point, whereas at subsequent cycles the converge at the end point of 300°C. This is therefore a product of the resistance heating method used, where the direct current applied produces an e.m.f. which, in this ferromagnetic material, results in a change in the lattice parameters. However the Curie temperature in these alloys is widely reported to be $\approx 110 \text{ }^\circ\text{C}$. This observation therefore poses a new question such as to whether these alloys shed their ferromagnetic properties completely or not.

The lattice parameters are shown for the first, second and fifth thermal cycle applied. It is notable that, whilst the lattice parameters at a given temperature are invariant with cycling, the transformation temperatures do evolve, by $\sim 8 \text{ }^\circ\text{C}/\text{cycle}$ for the austenite finish temperature A_f .

The evolution of the ETMT actuator position, along with the ex-situ DSC data, are shown in Figure 5.4. For comparison, DSC data for binary NiTi and two $Ni_{50}Ti_{35}X_{15}$ ($X=\text{Hf}$ or Zr) HTSMAs are also provided. The DSC results reproduce the observed TTs from the diffraction measurements and show a hysteresis (A_f-M_f) of around of 22 °C in cycle 5. The austenite finish temperature gradually declines on cycling, but the martensite TTs remain constant, which is unusual compared to NiTi SMAs. The ETMT actuator position is in effect a dilatometry measurement over the entire sample length (some of which remained cold and did not transform). The transformation on heating results in a contraction of the sample which is reversed on cooling, but there is an evolution in the end-point actuator positions with cycling that indicates a expansion of the sample from cycle 2 through 5. Since this occurs for the *fcc* austenite as well as the martensite, this cannot be due to the selection of preferred crystallographic variants and therefore must be due to the accumulation of plasticity, *i.e.* interface dislocations. By

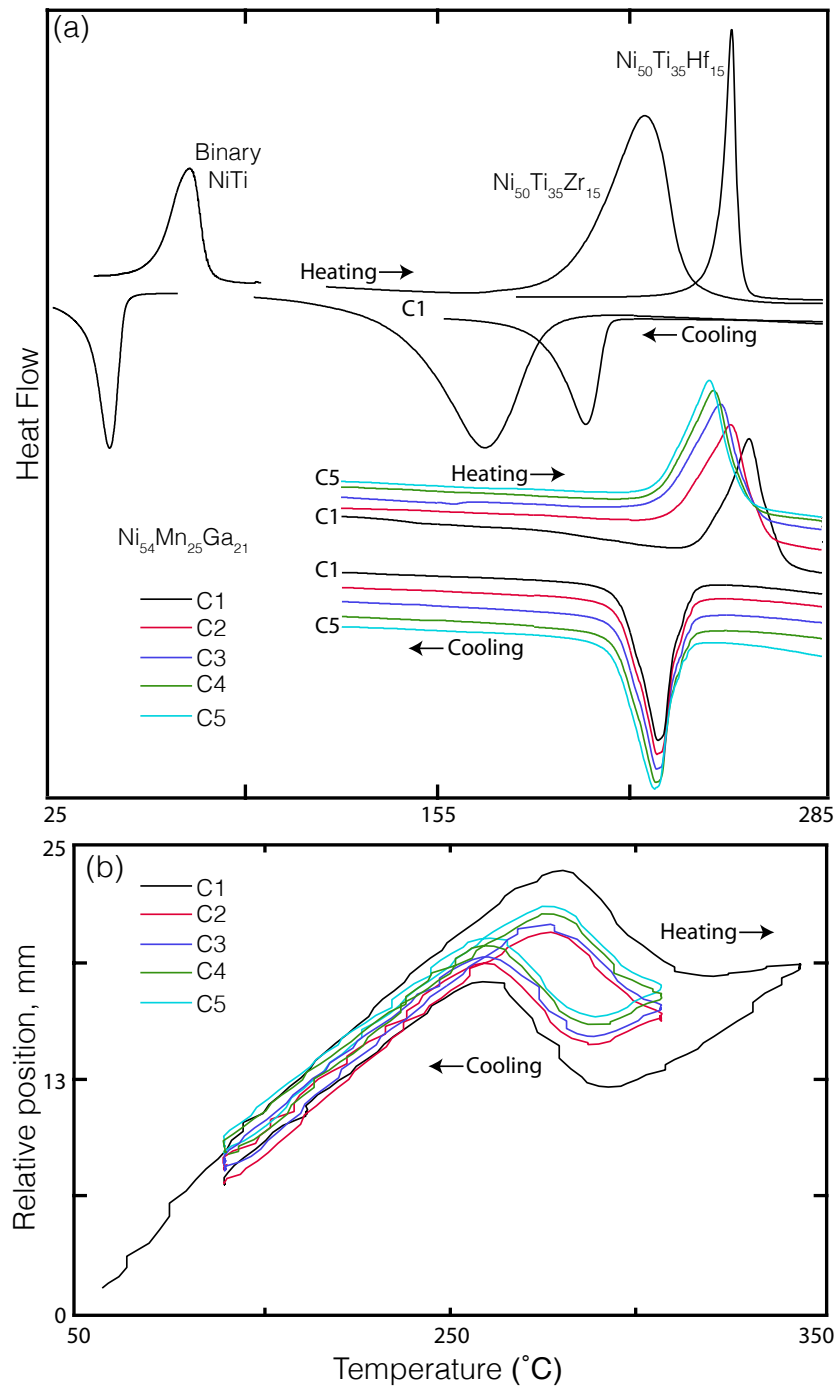


FIGURE 5.4: (a) Differential Scanning calorimeter (DSC) results obtained for five heating and five cooling cycles of as-rolled $Ni_{54}Mn_{25}Ga_{21}$ are shown here in comparison with the first cycle results for the low temperature a-cast binary NiTi and as-rolled high temperature $Ni_{50}Ti_{35}Hf_{15}$ and $Ni_{50}Ti_{35}Zr_{15}$ alloys and (b) Dilation in macroscopic $Ni_{54}Mn_{25}Ga_{21}$ along rolling (or tensile direction) during thermal cycling

reference to conventional NiTi SMAs, this would also be the reason for the gradual decline in the austenite transformation temperatures with cycling.

5.4 Summary and Conclusions

In summary, polycrystalline $Ni_{54}Mn_{25}Ga_{21}$ has been produced by a conventional ingot metallurgy and hot working approach. It is found to be a viable high temperature shape memory alloy material, albeit a brittle material with $M_f = 236$ °C. The lattice parameters measured in both phases were found to be affected by the magnetic fields induced in the specimen by the applied ohmic heating method used, even above the expected Curie temperature of the alloy. Some functional fatigue was observed in the austenite transformation temperatures on heating. The thermal expansion / contraction of the tetragonal martensite a_t and c_t cell parameters were observed to accelerate above the expected Curie temperature.

Chapter 6

Unexpected Lattice Instability around the Martensitic Transformation

Summary

Intermetallic shape memory alloys undergo a martensitic transformation from a high symmetry, high temperature phase to a low temperature, low symmetry phase. The transformation can be biased by application of a stress, gives rise to a shape and modulus change and shows a hysteresis. As long ago as the 1940s, Zener [Zener, 1948] suggested that lattices at the limit of stability would show very low modulus, and often a low energy phonon mode is observed in the direction of shear associated with martensite transformations. Here we show that the lattices of shape memory alloys change very significantly during transformation, and that this is a general effect observed in a range of thermal shape memory alloys. In addition, the thermal expansion coefficients of the martensite phase are often observed to be negative in some unit cell directions.

6.1 Introduction

In the phenomenological theory of martensite transformations [Lieberman et al., 1955], the high temperature B2 austenite phase in a shape memory alloy (SMA) such as NiTi is taken to transform, with one set of elastic moduli and lattice parameters, to a martensite phase that forms as self-accommodating, internally twinned variants as shown in Figure 6.1(a). The martensite phase may be orthorhombic (B19) , monoclinic (B19') or rhombohedral (R) [Otsuka and Ren,

2005]. Here we examine the cases of near-equiatomic $\text{Ni}_{49.8}\text{Ti}_{50.2}$ and the high temperature shape memory alloys $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$, $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ and $\text{Zr}_{50}\text{Cu}_{25}\text{Co}_{12.5}\text{Ni}_{12.5}$. Usually, the lattice parameters and elastic moduli of the participating phases in a martensitic transformation are taken to be invariant, excepting thermal expansion.

Diffusionless transformations are generally characterised by calorimetry, dilatometry or resistivity; these are bulk characterisation techniques that measure symptomatic properties and do not divulge any crystallographic information. Transmission electron microscopy (TEM) is therefore frequently used to characterise the variant relationship. However, observations made in thin foils by TEM may not be representative of bulk materials, for example in terms of transformation temperatures. Recently, neutron [Dunand et al., 1996; Qiu et al., 2011; Sittner et al., 2004; Ye et al., 2009] and synchrotron X-ray diffraction [Kulkov and Mironov, 1995; Paula et al., 2006] have become popular tools for examining these transformations in situ and in the bulk, allowing the effect of bias stress on the textures and lattice parameters to be examined, as well as the examination of, for example, detwinning of the martensite phase on application of a stress. However, often only a few temperatures are examined, because historically the counting times have been quite long, especially where neutron diffraction is used.

Displacive phase transitions proceed by shear of one lattice into another, and possibly an additional symmetry-breaking displacement of atoms within the unit cell (termed a Wyckoff shear [Obbard et al., 2010]). In such a situation, one or more of the phonon modes of the high temperature phase must decrease to zero, and therefore the elastic moduli in that direction also tend to reduce. Hence the C' shear modulus in SMAs undergoing the B19' transformation, for example, tends to be quite low.

Here, we use synchrotron X-ray diffraction (SXRD) to examine the evolution of the austenite and martensite lattices during the thermally induced transformation.

6.2 Experimental Description

Small ~ 60 g ingots were obtained by vacuum arc melting of pure elemental starting materials, homogenised at 900°C (800°C for $\text{Zr}_{50}\text{Cu}_{25}\text{Co}_{12.5}\text{Ni}_{12.5}$) for 24 hours and then hot rolled after encapsulation in a steel can at the homogenisation temperature. The $\text{Ni}_{49.8}\text{Ti}_{50.2}$ alloy preparation has been reported before [Jones and Dye, 2011]. A fine grained microstructure was obtained that enabled complete Debye-Scherrer rings to be obtained from the volume sampled during SXRD of $0.4 \times 0.3 \times 1.5$ mm. 1.5 mm thick dogbone shaped samples of 15 mm gauge length and 1.5 mm width were obtained by electro-discharge machining and wet grinding. SXRD experiments were performed using the monochromatic beamline ID15B at ESRF, France.

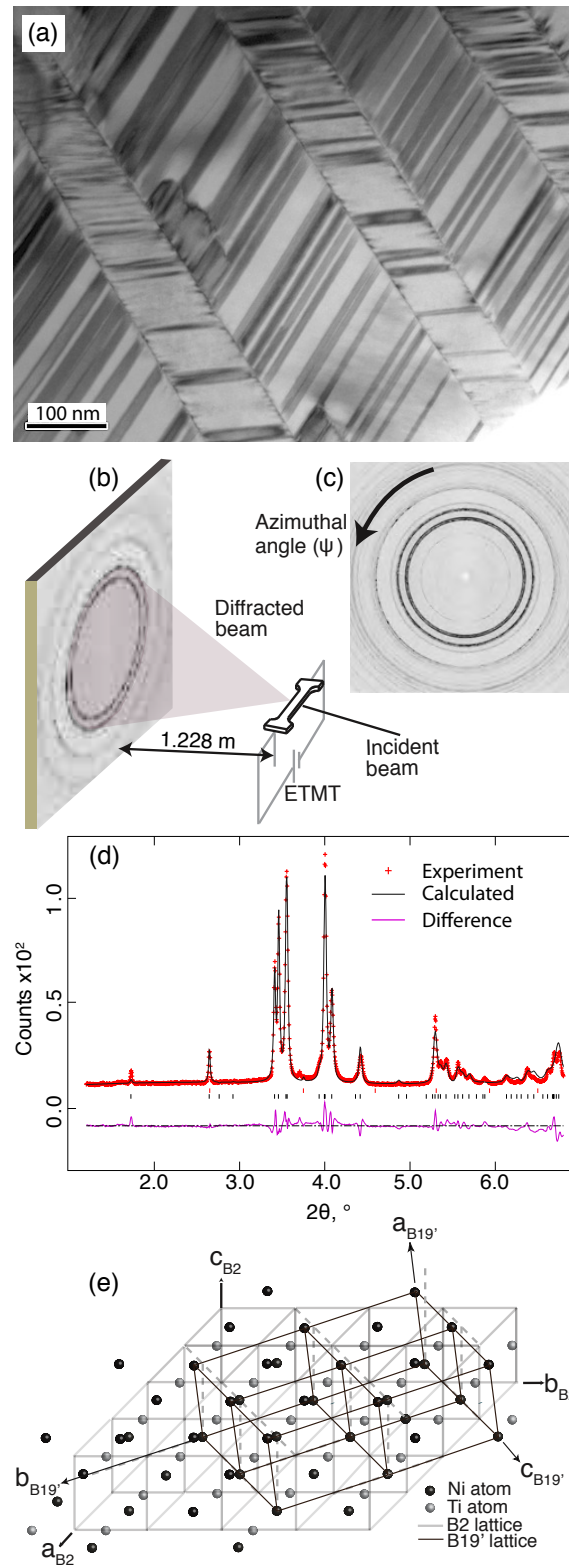


FIGURE 6.1: (a) Self accommodating martensite twins in $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$ (bright field TEM), (b) synchrotron X-ray diffraction experimental setup (c) diffraction pattern at showing B19' rings in $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$, (d) X-ray diffraction spectra; integrating intensity across the complete diffraction rings in (c), and (e) schematic illustration of the orientation relationship in a $\text{B2} \leftrightarrow \text{B19'}$ martensitic transformation.

Samples were resistance heated along the gauge length under 5 MPa load (50 MPa for NiTi) using an Instron Electro-Thermo-Mechanical Tester (ETMT). The diffraction information was obtained in transmission mode using a 0.1427 Å X-ray beam and a Pixium 4700 area detector placed 1.228 m from the sample, Figure 6.1b. Adequate diffraction images, Figure 6.1c, could be obtained in 0.4 s during heating and cooling at a rate of 1 °Cs⁻¹. Intensity (integrated across 360° azimuthal angle) *vs.* diffraction angle (2θ) patterns, Figure 6.1d, were obtained from the 2D images by using FIT2D [Hammersley et al. \[1996\]](#) and each pattern was Rietveld refined [[Rietveld, 1969](#)] using the General Structure Analysis System (GSAS) [[Larson and Von Dreele, 1994](#); [Toby, 2001](#)] to evaluate the lattice parameters and volume fractions of each phase.

6.3 Results and Discussion

The motif where γ is taken to be the monoclinic angle [[Huang et al., 2003](#)] has been adopted in the present investigation. The primary room temperature phase or martensite in all four alloys was observed to be P2₁/m monoclinic (B19'). The lattice correspondence between B19' and B2 is illustrated in Figure 6.1e. In Zr₅₀Cu₂₅Co_{12.5}Ni_{12.5}, a centered monoclinic (Cm space group) superstructure phase of atom fraction of < 0.005 was also observed with its peaks predominantly appearing as protrusions to the primary B19' peaks. The Cm lattice parameters were refined to be $a = 6.668 \pm 0.019$ Å, $c = 5.308 \pm 0.013$ Å, $a = 8.838 \pm 0.025$ Å and $\gamma = 104.420^\circ \pm 0.372^\circ$; the uncertainties in the refinement are relatively large due to the low fraction of the phase observed. The presence of the Cm phase in Zr intermetallics was first reported in the binary ZrCu alloy [[Firstov et al., 1997](#); [Seo and Schryvers, 1998](#)]. It has been observed that addition of Ni in Zr₅₀Cu₂₅Co_{25-X}Ni_X ($X = 15 - 25$ at.%) increases the volume fraction of Cm; rendering it the primary martensite phase for Ni additions of > 20 at.% [[Firstov et al., 1997](#)].

The evolution of the lattice parameters and fractions of each phase during heating and cooling in the 5th thermal cycle are shown in Figure 6.2 for Ni_{49.8}Ti_{50.2} and Ni₅₀Ti₃₅Hf₁₅. The usual thermal hysteresis is observed with hysteretic widths of 57 °C and 38 °C respectively; this hysteresis is associated with the interface plane strain and is minimised when the interfaces become completely compatible, according to the theory of martensite crystallography [[Cui et al., 2006](#)]. At all temperatures, the B19' lattice parameters excepting $c_{B19'}$ are larger in Ni₅₀Ti₃₅Hf₁₅ than in Ni₅₀Ti₅₀. The linear change in lattice parameter on heating and cooling away from the transformations is naturally interpreted as being due to thermal expansion; therefore the negative change in $b_{B19'}$ with temperature suggests a negative coefficient of thermal expansion (α_{th}) in this cell direction.

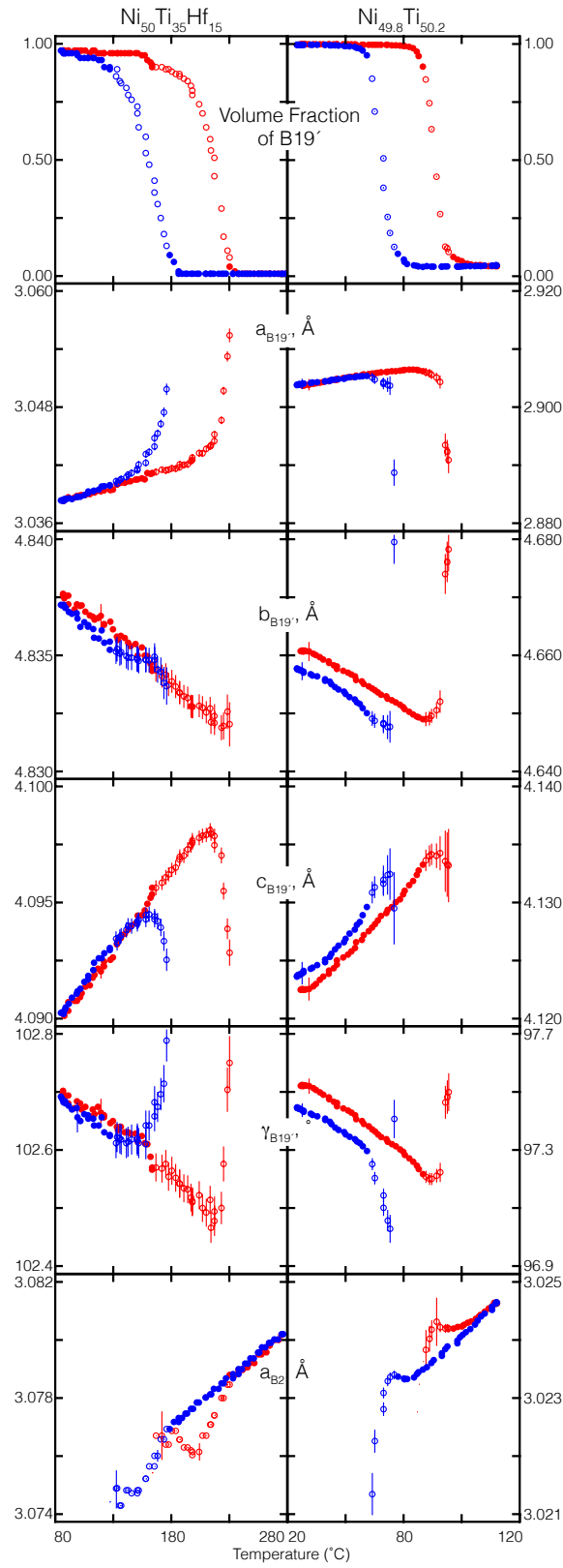


FIGURE 6.2: Evolution of B19' and B2 lattice parameters in $\text{Ni}_{49.8}\text{Ti}_{50.2}$ and $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$ during thermal cycling. Red symbols indicate heating, blue cooling; solid symbols are in the single phase region and open symbols during transformation. The Rietveld refinement fitting uncertainties are indicated.

During transformation, large changes are observed in both alloys. For example, in $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$ through the transformation (190–230°C) $a_{\text{B}19'}$ increases by 0.016 Å more than would be expected from thermal expansion alone. In contrast, $b_{\text{B}19'}$ shows very little additional change whereas $c_{\text{B}19'}$ shows a negative change. Startlingly, the $\gamma_{\text{B}19'}$ shear angle also changes, by in excess of 0.3°. The changes are most pronounced towards the end of transformation, and are repeatable between heating and cooling, with similar end-points being reached.

This observation is general and repeated in a near equiatomic binary alloy. However the sign of change alters for different alloys. For example, the change in $a_{\text{B}19'}$ is negative in $\text{Ni}_{49.8}\text{Ti}_{50.2}$ whereas it is positive for $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$. The $\text{B}19'$ cell volume also increases slightly during transformation on heating, by around 0.117 Å³ from 58.802 Å³, or 0.12%. In turn, in $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$ the B2 unit cell decreased in size during transformation from around 3.0785 Å by 0.0012 Å, which is a volume change of 0.12%. Using the B2 elastic moduli of $C_{11} = 130$ GPa, $C_{12} = 98$ GPa and $C_{44} = 34$ GPa [Brill et al., 1991] gives a bulk modulus of 109 GPa, so if this volume change were due to accommodation stresses, the average pressure would be on the order of 130 MPa.

One hypothesis as to the source of these large changes is that they are due to mechanical accommodation between the two phases, which will be influenced by the rolling texture and variant selection. In the loading direction, such changes to individual peaks have in fact been observed before in similar Ti-rich, near-equiatomic NiTi for diffraction measurements made in the loading direction only [Sittner et al., 2004]. However, the changes might be expected to be orientation-dependent, and modelling suggests that the strains would be on the order of 2×10^{-3} [Novák and Sittner, 2004].

To examine orientation dependence, Figure 6.3 shows the evolution of the (001) and (010) $\text{B}19'$ peaks in the rolling and normal directions of the sheet, so as to evaluate whether the texture, and hence accommodation stresses, are the primary cause of the deviations during transformation or whether these are intrinsic to the behaviour of the crystal in the vicinity of transformation. The scatter in the data is of course greater due to the poorer grain sampling than for the full-ring whole-pattern refinements in Figure 6.2. However, it is clear that the (001) $\text{B}19'$ behaves the same in both directions. The (010) $\text{B}19'$ lattice parameter is not equal to the $b_{\text{B}19'}$ due to the monoclinic shear γ ; however the negative α_{th} is observed and there are no large deviations (> 0.002 Å) from linearity, as for the $b_{\text{B}19'}$. This uniformity of the behaviour of these two peaks supports the hypothesis that the deviations observed in Figure 6.3 are mostly due to deviations in the lattice and not transformation stresses.

Of course, the first martensite to form, with relatively little surplus undercooling and therefore driving force for transformation, should in principle be closer to its natural, unstrained condition. Then, as the driving force increases the martensite twins can expand, expending more energy on

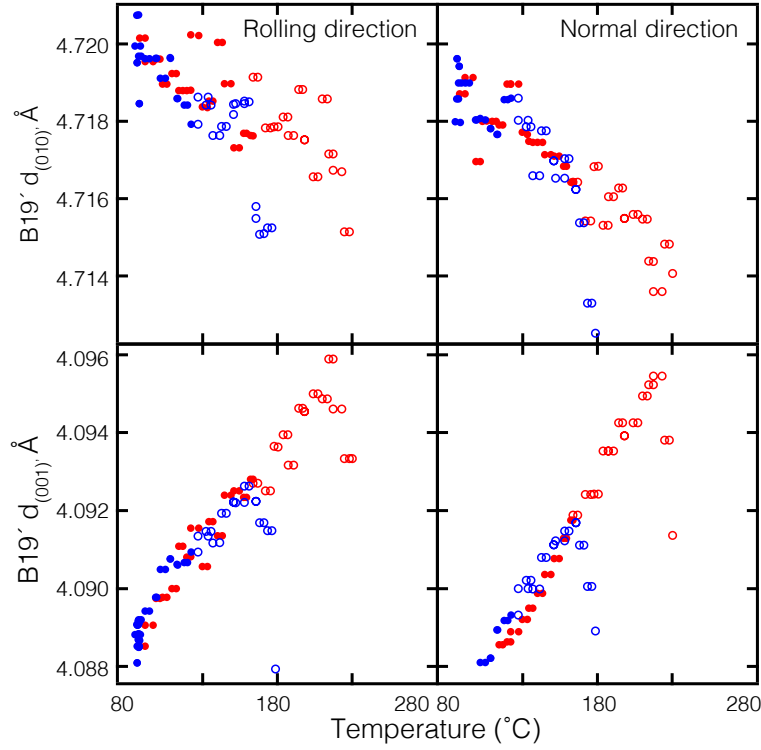


FIGURE 6.3: Evolution of the lattice parameters in 10° segments of the diffraction rings in the 0° (rolling direction) and 90° (normal direction) locations, for $\text{Ni}_{50}\text{Ti}_{35}\text{Hf}_{15}$ on heating and cooling during the 5th thermal cycle and for the (010) and (001) diffraction peaks.

elastic straining of the surrounding material and, where these strains are large, in defects (*i.e.* interface and other dislocations). This gives rise to the hysteresis in transformation temperatures that is normally observed.

Data for another two shape memory alloys, $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ and $\text{Zr}_{50}\text{Cu}_{25}\text{Co}_{12.5}\text{Ni}_{12.5}$, are shown in Figure 6.4. If we interpret the deviations as strains using the maximum deviations from linear thermal expansion, Table 6.1 is obtained. These strains, in particular the large $\gamma_{\text{B19}'}$ angle change in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$, are quite large and, if interpreted as stresses using recent calculations for the B19' elastic constants [Wagner and Windl, 2008], would be similar to those at yield. For example, if the martensite yield stress is on the order of 1 GPa and using a modulus of 90–145 GPa for the B19' in different directions [Qiu et al., 2011], the yield strain is $7\text{--}11 \times 10^{-3}$.

TABLE 6.1: Maximum strain ($\times 10^{-3}$) during heating along individual crystallographic axes in $\text{Ni}_{49.8}\text{Ti}_{50.2}$, $\text{Ni}_{35}\text{Ti}_{50}\text{Hf}_{15}$, $\text{Ni}_{35}\text{Ti}_{50}\text{Zr}_{15}$ and $\text{Zr}_{50}\text{Cu}_{25}\text{Co}_{12.5}\text{Ni}_{12.5}$

	NiTi	NiTiHf	NiTiZr	ZrCuCoNi
$a_{\text{B19}'}$	-6	+4	+6.5	-3.4
$b_{\text{B19}'}$	+5	0	+1	-8.5
$c_{\text{B19}'}$	0	-5	0	-12.5
γ	+3	+3	+12	-3.4

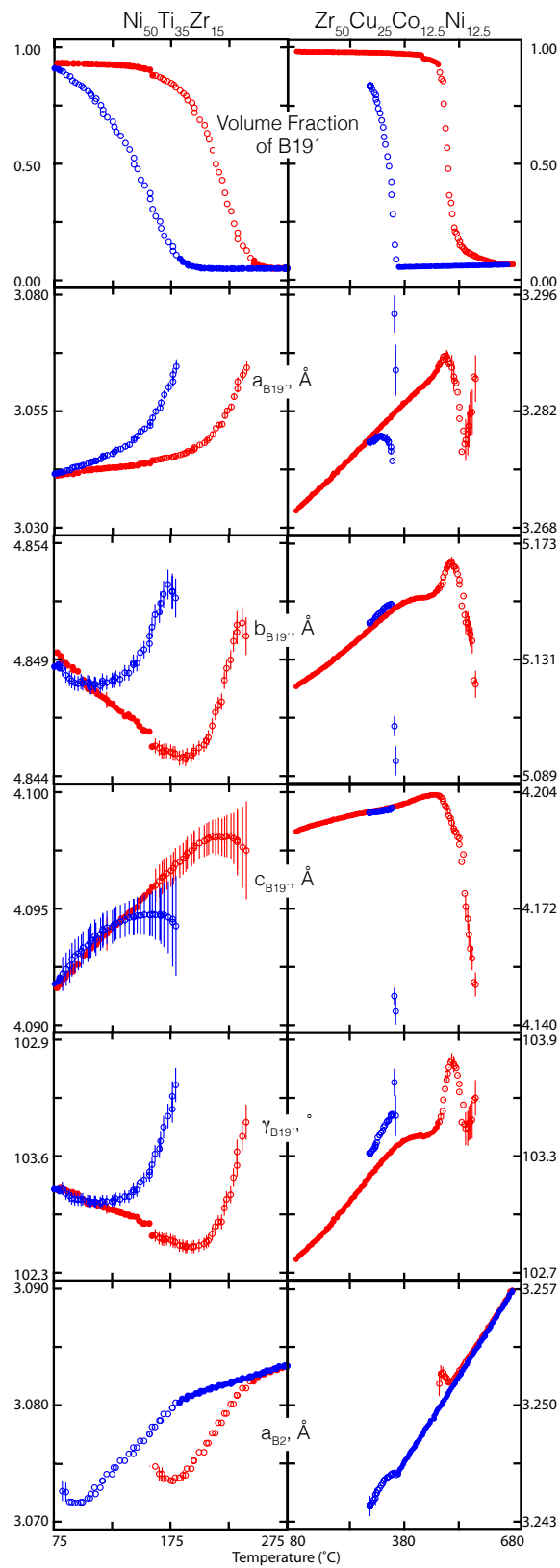


FIGURE 6.4: Evolution of B19' and B2 lattice parameters in $\text{Ni}_{50}\text{Ti}_{35}\text{Zr}_{15}$ and $\text{Zr}_{50}\text{Cu}_{25}\text{Co}_{12.5}\text{Ni}_{12.5}$ during first thermal cycle. Red symbols indicate heating, blue cooling; solid symbols are in the single phase region and open symbols during transformation. The Rietveld refinement fitting uncertainties are indicated.

Surprisingly, the directions of the deviations are not towards the ideal B2/B19' lattice relationship, as might be expected if these were simply mechanically-induced deformations in a continuous shearing process from one structure to another, in a naive interpretation of Zener's suggestion. In the NiTiHf alloy, $a_{\text{B19}'}$ is smaller than a_{B2} by 1.1% at the start of transformation on heating, and the lattice expands by 0.4% during transformation, as might be expected. In contrast, $b_{\text{B19}'}$ is 11.1% bigger than $\sqrt{2}a_{\text{B2}}$ and $c_{\text{B19}'}$ 5.8% smaller before transformation, but no change in $b_{\text{B19}'}$ is observed while $c_{\text{B19}'}$ shrinks further. During dissolution the shear angle $\gamma_{\text{B19}'}$ actually increases, rather than moving towards 90° . Similar deviations away from the B2 state are observed in the other alloys, but in different directions.

An alternative to the mechanical hypothesis would be that the equilibrium lattice parameters of the martensite and austenite phases are rather different away from the transformation than in the vicinity of transformation. As implied by Zener, it might be possible that the elastic constants of the B19' phase are smaller around the transformation point than at temperatures where either phase is completely stable, although this seems unlikely. Since these transformations are displacive and soft phonon-mediated, with the B2 phase being phonon-stabilised, this would be consistent with a Zener's original perspective that shear transformations are undergone by lattices at the edge of stability.

This hypothesis has quite important consequences for the popular phenomenological theory of martensite transformations (PTMT) used by materials scientists in alloy design [Cui et al., 2006]. In this approach, the lattice parameters are used to calculate the transformation stretch matrix for the nominal orientation relationship, and then the relative fractions of a twin pair, their orientation to the matrix and the principle strains at the interface are calculated from its eigenvalues λ_i . The middle eigenvalue is then interpreted as the interface plane strain, which must be 1 for a perfect, unstrained interface. It is observed that the temperature hysteresis is minimised as λ_2 approaches 1. This opens the way to alloy design using simple concepts such as Vegard's Law. However, if the lattice parameters measured for each phase away from the TTs are inappropriate these calculations of λ_2 will not necessarily be a perfect guide for alloy designs that minimise transformation hysteresis. In addition, even if these calculations were corrected, the calculations of strain energy that arise from the PTMT approach will likely be too high if the elastic constants of the phases are lower in the easy shear transformation regime.

In the density functional theory literature, it is suggested that the B19' phase would require shear stresses in excess of 1 GPa to be stabilised relative to the B33 structure [Wagner and Windl, 2008], which seems unreasonably large. It has been suggested that the B19' may be entropically stabilised by phonons [Wagner and Windl, 2008]. The present data suggest that large elastic lattice changes (strains) do in fact evolve during transformation.

6.4 Conclusions

In conclusion, large changes (up to 1%) in lattice parameter are observed in shape memory alloys during transformation. If the lattice parameters and elastic constants that obtain away from the transformation regime are assumed, these strains would correspond to very large stresses. This is consistent with the idea that during displacive transformations lattices are at the edge of stability and therefore can shear substantially. In addition, the thermal expansion coefficients of the $b_{B19'}$ direction in NiTi based alloys are observed to be negative.

Chapter 7

Conclusions and Further Work

7.1 Conclusions

The motivating question in this research project was “can high temperature shape memory alloys be produced that have the possibility of being useable in structural, many-cycle actuator applications?” By this it is meant that the mechanical properties are reasonable (stiffness, usable strength), that a conventional ingot metallurgy processing route can be obtained to produce polycrystalline material and that the alloy has some toughness and fatigue capability. A number of alloy systems have been evaluated, and the following conclusions drawn.

15 at.% substitutions of Hf or Zr for Ti in NiTi were initially attempted. Both additions were found to raise the transformation temperatures. Taking conventional near-equiatom NiTi to have an M_f of around 56°C and a hysteresis $A_f - M_f$ of 32°C from [Jones and Dye \[2011\]](#) , then 15 at.% Hf raises M_f to 188°C and the hysteresis to 69°C, based on DSC measurements. Zr was found to be brittle on hot rolling, with a 20°C lower A_f and a hysteresis of 113°C. 3 at.% Cu substitutions for Ni were found to lower the transformation temperatures very substantially.

In situ synchrotron X-ray diffraction measurements showed greater sensitivity to the final stages of transformation and consequently larger hysteresis. Difficulties with the thermocouples calibration in the experiment made absolute measurements of the temperatures more problematic and so in terms of absolute values, the DSC measurements are preferred. The resistance heating setup used allows crude dilatometry to be performed, which showed relatively small dilatations from the -HfCu alloy. This reduced mechanical hysteresis was not reflected in the transformation temperature per-cycle drift or thermal hysteresis of the alloys. It should also be noted that the HTSMAs examined here showed much larger per-cycle transformation temperature drift than near-equiatom NiTi. It was also found that the transformations in the -Hf and -Zr

containing HTSMA candidates proceeded much more gradually than in near-equiatomic NiTi - on the order of 50-80°C for the on-cooling martensite transformation compared to on the order of 10°C in NiTi.

In contrast, much greater TTs were obtained in $\text{Zr}_2\text{Cu}(\text{Co}_{0.5}\text{Ni}_{0.5})$, with M_f above 290°C. The hysteresis $A_f - M_f$ is, however, over 190°C and the martensite thermal expansion coefficients in the different cell directions varied from 29 to $88 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, which is relatively large for an engineering material. M_f was found to be quite stable over five thermal cycles, but A_f declined by approx. 11°C per cycle.

The ferromagnetic Ni_2MnGa Heusler alloy was also examined with the off-stoichiometric composition of $\text{Ni}_{54}\text{Mn}_{25}\text{Ga}_{21}$, as a possible thermal shape memory actuator. M_f was found to be 232°C, with hysteresis $A_f - M_f$ of 66°C. Cyclic stability of M_f was again observed but A_f declined by around 8°C over the first five thermal cycles. For both of these alloys, $\text{Ni}_{54}\text{Mn}_{25}\text{Ga}_{21}$ and $\text{Zr}_2\text{Cu}(\text{Co}_{0.5}\text{Ni}_{0.5})$, the stability of A_s would suggest that A_f will gradually stabilise and therefore that long-term cyclic stability is a possibility. In particular, by cycle five the hysteresis $A_f - M_f$ had decreased to 22°C, lower than conventional NiTi.

Thus $\text{Ni}_{54}\text{Mn}_{25}\text{Ga}_{21}$ appears to be an appealing potential HTSMA. However, on loading the samples were found to have a strength of less than 100 MPa even though hot rolled polycrystalline strip could be produced. It is perhaps unsurprising that a 3-sublattice intermetallic is brittle, but there are ongoing efforts to develop this system into a viable engineering material.

More broadly, the major finding of this research was that both NiTi-based alloys and $\text{Zr}_2\text{Cu}(\text{Co}_{0.5}\text{Ni}_{0.5})$ showed both negative thermal expansion coefficients in the B19' phase in certain directions and very significant lattice parameter deviations (up to 1%) during transformation. Neutron measurements in specific texture and loading directions have previously observed this effect and some of it (0.2%) can be attributed to accommodation stresses, but in the present work they are observed in all texture directions with a consistent magnitude. This is therefore suggestive that something more than mechanical accommodation might be the cause of this effect.

One possibility is that the equilibrium lattice parameter of the forming phase might be evolving with the undercooling driving force for transformation so as to minimise the surface energy associated with growing ultra-fine laths. Another might be that the elastic constants of a lattice at the edge of stability are different, although this seems physically unlikely. In any case, given recent work suggesting that the shear strain required to stabilise the B19' compared to the B33 martensite in NiTi is quite large, the observation of such large deviations does at least suggest that such large shears may occur.

In contrast, no such deviations were observed in $\text{Ni}_{54}\text{Mn}_{25}\text{Ga}_{21}$ on thermal cycling.

It is also worth reviewing the major technological achievements in this project. At the beginning of this project there was no extant expertise at Imperial in novel alloy vacuum arc melting or hot working using encapsulated steel cans. Such expertise is now a core part of the research group. Similarly, this was the first shape memory alloy project initiated in the group. Therefore a process route and alloy development pathway has been developed over the course of this work. Necessarily, this project has therefore involved an exploration of different techniques (such as TEM and EPSC modelling), which generally tend to be more challenging in materials with monoclinic crystal structures than in more familiar cubic and hexagonal metals such as nickel superalloys and titanium alloys.

7.2 Suggestions for Further Work

The work here does suggest that HTSMA's are possible. Development of a micromechanical understanding of the alloy behaviour will be required to further progress this work, starting with a calculator for the transformation distortion matrix eigenvalues and hence the orientation relationships and interface strains. Application of Vegard's law and first-order literature-based linear extrapolation of the transformation temperatures should then allow HTSMAs with minimal hysteresis to be suggested for the NiTi system. It seems likely that these will consist of Hf additions on the order of 15+ at.% and quaternary+ additions of Ni-substituting elements to minimise λ_2 , at a cost in transformation temperatures. The initial work here suggests that $\text{Zr}_2\text{Cu}(\text{Co}_{0.5}\text{Ni}_{0.5})$ may provide a more promising basis than NiTi, but this alloy system is relatively unknown and therefore significant effort would be required to determine the correct additions to use to minimise hysteresis. Stoichiometry adjustment of the Zr and Cu fraction might be another promising route.

Over the course of this project, other workers have started to make significant progress in the micromechanical modelling of the variant relationships necessary to assess, e.g. the effect of stress on the transformations in the mixed temperature-stress cycling that occurs in real bias spring actuators. Such developments are probably a necessity to be able to optimise and perform lifing calculations in real devices in safety-critical applications.

For the alloys prepared here, their mechanical properties (moduli, stress-strain curves, effect of bias stress on thermal cycling, etc.) have not been extensively characterised over the course of this project, and would ultimately be required.

Much of the NiTi community, especially those concerned with ‘bio-inspired’ shape memory wire structures, has instead pursued the use of plastic deformation and fine intermetallic precipitates to nucleate the martensite the forms in an attempt to stabilise the product produced. This approach is not viewed as likely to succeed completely in stabilising the alloys, especially where more substantial product forms such as sheet or plate are required. However, the use of intermetallics to place the NiTi at the phase boundary and therefore keep the NiTi stoichiometry constant in the presence of melt-to-melt composition variations is viewed positively in view of the extremely tight composition required to minimise hysteresis and λ_2 found by [Cui et al. \[2006\]](#). Whether the optimisation can survive the imposition of yet another constraint, is however, another matter, and this may therefore limit the industrial feasibility of any proposed ‘optimal’ alloys.

It should also be noted that thermal shape memory alloys are only a subset of the materials that use a phase transformation to achieve a functional effect. Other materials such as the Ni_2MnGa , $\text{NiMnCO}(\text{In},\text{Sn})$ and FeMnGa systems are of increasing interest for magnetocaloric and elastocaloric applications, such as solid-state magnetic refrigeration as well as in magnetic actuators. In the refrigeration domain, it has been suggested that this would allow the production of heat pumps with coefficients of performance in excess of five, well above the level at which the replacement of gas fired plant with air-source heat pumps becomes attractive for the production of domestic low-grade heat, even with present CO_2 -laden electricity production in much of Northern Europe. This would allow the changeover of domestic heating to occur in tandem with the decarbonisation of the electricity grid rather than following decarbonisation, hastening the transition to a low- CO_2 society.

Therefore the extension of this work to examine hysteresis effects and the micromechanics of polycrystalline materials that transform to achieve a functional effect would also represent a fruitful topic of further work.

Appendix A

Micromechanical Modelling of Microstrains and Twinning in Alpha Brasses

Summary

The deformation micromechanics of two conventionally extruded and recrystallized α -brasses containing 3 and 15 wt.% Zn was investigated *via* the accumulation of intergranular microstrains measured by in-situ neutron diffraction experiments. The lattice and overall macroscopic tensile stress-strain behaviour were simulated using an improved Elasto Plastic Self-Consistent (EPSC) modelling scheme [Clausen et al., 2008]. In both alloys, the maximum lattice strain along the extrusion axis was found to accumulate on grains with their {200} crystallographic planes parallel to the tensile/extrusion direction. The predicted residual strain distribution in Cu-3Zn alloys at lower strains ($\approx 1\%$) was noticeably different from that observed at higher strains. In the model, twinning was predicted to occur from the beginning of deformation in the Cu-15Zn alloy, whereas in the Cu-3Zn alloy an accumulation of lattice strains in twinning-oriented grains was required over the course of the first 1% of plastic deformation before twinning could begin. In this alloy, twinning was only predicted to be a significant deformation mechanism between 7 and 11% plastic strain, after which it was predicted to saturate.

A.1 Introduction

α brasses, that is *fcc* Cu alloys with varying Zn content, have long been of theoretical interest because the stacking fault energy decreases with Zn content, increasing the propensity for partial dislocation formation and the formation of $\langle 112 \rangle \{111\}$ twins. Increasing Zn content therefore gives rise to two effects; an increase in yield strength due to solution hardening and an increase in work hardening rate as twinning progresses.

Over the last 25 years, it has become increasingly common to examine the intergranular stresses that arise in materials as a consequence of plastic deformation produced when grains in differing orientations yield at different applied stresses during the early stages of plasticity using diffraction-based techniques. Here, the peak shift that arises due to elastic strain is identified with a strain, averaged over grains with a common plane normal orientation. In the earliest work [Clausen, 1997], single phase *fcc* materials deforming by slip were examined and it was found that the intergranular stresses must be accounted for when making measurements of macroscopic stress. In addition, the intergranular stresses have been found to be a sensitive tool for developing our understanding of the micromechanisms of deformation, by reference to polycrystal models of deformation - either finite element models such as those of Staroselsky and Anand [1998], Dawson et al. [2002] and Dunne et al. [2007b,a], or self-consistent models such as those developed by Turner and Tomé [1994].

However, modelling the mechanical behaviour of two phase materials and the incorporation of the effect of twinning [Kalidindi, 1998] has been found to be more problematic. Twinning is of particular interest because it proceeds *via* lattice shear and is analogous to a shear phase transformation, such as martensite formation in steels and shape memory alloys. During twinning, the parent matrix and twin lattices form a mirror reflection in a plane or they are related by a 180° rotation about an axis; these misorientations are often equivalent in high symmetry crystals. Accordingly there exists a invariant plane (K_1), which also contains the principal shear direction n_1 . The other invariant (or conjugate) plane is K_2 and the conjugate shear direction n_2 is the intersection of K_2 and a plane P which also contains the shear direction n_1 and the normals to planes K_1 and K_2 . A detailed investigation of the geometric and crystallographic characteristics of deformation twinning are presented by Christian and Mahajan [1995]. It has been assumed [Lebensohn and Tomé, 1993] that a certain critical stress on the habit/twinning plane is a necessary condition for the activation of twinning in a given crystallographic structure. When twinning occurs, it results in a large reorientation compared to the parent grain. The reorientation results in a shear strain along the twinning direction in the habit plane which can relieve the applied mechanical strain in the parent grain, even once accommodation strains are taken into account [Wu et al., 2008].

In the previous version [Turner and Tomé, 1994] of EPSC scheme strain and stress compatibility within the grain was not enforced. The simulated results were in fairly good agreement with the experimental measurements in Zr but were less predictive in certain cases, *e.g.* in Mg alloys [Agnew et al., 2003, 2006]. Recently, Clausen et al. [2008] have significantly refined their description of twinning within the Eshelby self-consistent modelling framework to enforce compatibility at the twin/parent interface and compared their model to intergranular strain measurements in the single phase hexagonal Mg alloy AZ31. Their prediction of the evolution of texture, the macroscopic stress-strain curve and the elastic lattice strain response during deformation were in good agreement with the experimental observations. They observed an abrupt change in texture with twin reorientation, unusual hardening and a rapid stress relaxation in grains that underwent twinning. However, twinning in *fcc* metals has not yet been examined in a similar fashion. Compared to an *hcp* metal, *fcc* materials provide a more isolated test because there are no complications that arise due to anisotropic thermal contraction and there is only one slip system. Also, previous work [Cho et al., 2002] has shown that $\{11\bar{2}3\}$ slip can appear similar to twinning in its effect on the microstrains in α -Ti.

In the present paper, we examine the behaviour of two α brasses, first a Cu-3Zn (wt%) brass that shows relatively little propensity to twin, and second a Cu-15Zn brass that twins relatively significantly. The intergranular strains measured using neutron diffraction are compared to those predicted by a self-consistent model.

A.2 Experimental

The 3 and 15 wt.% Zn samples used in this study were vacuum induction melted from billets of pure copper and zinc at McMaster University, Ontario, Canada, then homogenized, extruded into 0.5 in. diameter rods and recrystallised in the range of 750-790 °C by Nu-Tech, Arnprior, Ontario, Canada. The grains sizes were measured by the linear intercept method along and perpendicular to the extrusion axis in sections parallel to the direction of extrusion. For *in situ* tensile tests, threaded dogbone shaped specimens with a gauge length of 20 mm were machined with their tensile axis parallel to the extrusion axis.

A.2.1 In-Situ Strain Measurement

In-situ neutron diffraction strain measurements of the evolution of lattice strain during deformation of the two alloys were performed on the N5 and L3 spectrometers of the National Research Council of Canada at the NRU reactor, Chalk River, Ontario, Canada. Monochromation of

the incident beam was achieved using the $\{115\}$ reflection of a Ge high-mosaic single crystal at take-off angles ($2\theta_m$) of 80° and 92° , providing a monochromatic incident beam to the sample of $1.6685\text{\AA}$ and $1.5675\text{\AA}$, respectively. The relative uncertainty in the wavelength calibration from a standard nickel powder was $\approx 30 \times 10^{-6}$.

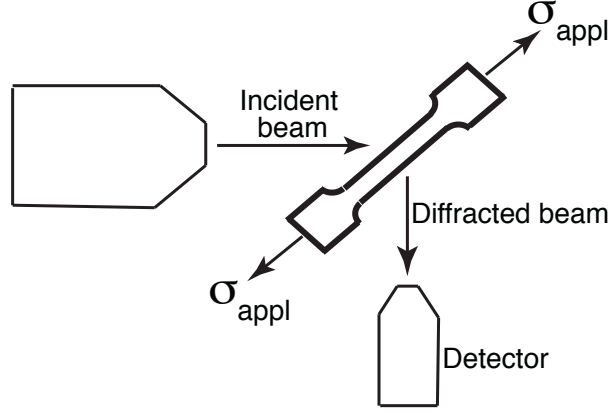


FIGURE A.1: Schematic of the neutron diffraction experimental setup for capturing lattice strains in longitudinal direction

The d_{hkl} -spacing of a set of grains in a given crystallographic orientation $\{hkl\}$ to the scattering vector $\mathbf{Q}$ is given by Bragg's Law, $\lambda = 2d \sin \theta_{hkl}$, where λ is the wavelength and $2\theta_{hkl} = \phi$ is the scattering angle. This allows the strain at the j th measurement point in the i direction to be estimated from $\varepsilon_{hkl}^{i,j} = \Delta d_{hkl}^{i,j} / d_{hkl}^{i,0}$, where $d_{hkl}^{i,0}$ is the strain-free lattice parameter. This expression can be re-formulated to give $\varepsilon_{hkl}^{i,j} = -\Delta \theta_{hkl}^{i,j} \cot \theta_{hkl}^{i,0}$. Therefore, an absolute measurement of wavelength is unnecessary except in so far it allows the recognition of any ϕ_0 offset which may cause errors *via* the $\cot \theta$ term. The general arrangement of the experiment is shown in Figure A.1.

A 50kN screw-driven load frame was used, allowing measurements to be made both at load and after unloading; macroscopic strain was captured using an extensometer. The load rig was oriented to permit measurements with the scattering either along or transverse to the loading direction. The diffraction peaks obtained were fitted to a Gaussian distribution with a flat background. The measurements were performed using the $\{222\}$, $\{200\}$ and $\{311\}$ diffraction peaks. The $\{220\}$ peak did not have enough intensity for good statistical grain sampling in the longitudinal direction; therefore the lattice strain measurements possessed high scatter and are not presented here.

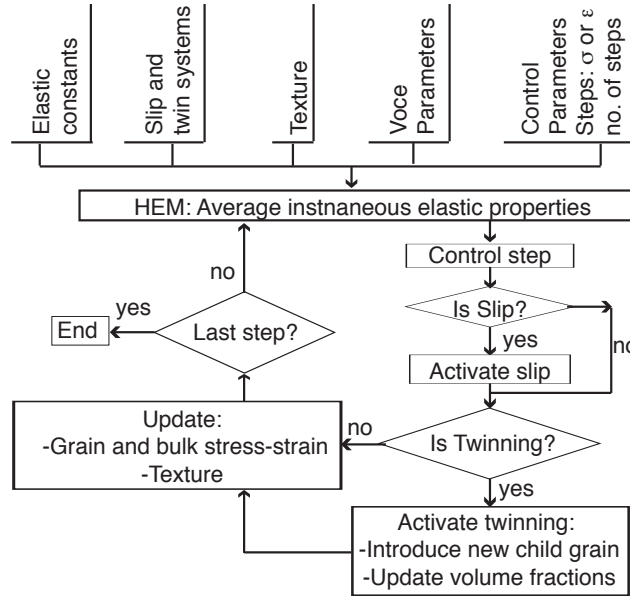


FIGURE A.2: Algorithmic schematic of the current EPSC scheme

A.2.2 Modelling methodology

The Eshelby self consistent modelling approach first described by Hutchinson [1970] is based on the plasticity approach of Taylor [1938], Bishop and Hill [1951], Hill [1965a,b, 1967] and implemented by Turner and Tomé [1994]. The approach has been extensively detailed elsewhere [Raghunathan et al., 2007]. Here, the implementation of twinning first by Turner *et al.* [Turner et al., 1995] and in an improved fashion by Clausen et al. [2008] will be briefly described.

An algorithmic schematic of the current EPSC formulation is shown in Figure A.2. At the core of this phenomenological modelling approach is Eshelby's equivalent grain/inclusion formalism which is fundamentally based on the proof that the strains in an ellipsoidal grain are uniform throughout the grain [Eshelby, 1957]. It is assumed that all grains, 1) have an elliptical shape, 2) identical size, i.e., the major and minor axis have same dimensions in all grains and 3) that grain interactions can be approximated *via* the response of an average homogenous effective medium (HEM). In the elastic case, the medium stiffness is evaluated by averaging the elastic strains in all the inclusions/grains, based upon an initial estimate obtained from the single crystal elastic constants and the texture of the material. This is extended to plastic regime by expressing the solution in incremental (rate) form and introducing the concept of instantaneous modulus which relates the stress rate ($\dot{\sigma}$) and strain rate ($\dot{\epsilon}$) by $\dot{\sigma} = C : \dot{\epsilon}$, where C is the overall average instantaneous stiffness. Similarly, the constitutive equation for a single grain can be written as $\dot{\sigma}^c = C^c : \dot{\epsilon}^c$, where c denotes an individual grain. The grain modulus C^c is a function of the orientation of the grain and its instantaneous plastic state. Eshelby showed

that the total strain in the grain is related to that of the bulk medium by $\dot{\epsilon}^c = A^c : \dot{\epsilon}$, where A^c is an accommodation tensor derived from the Eshelby solution [Raghunathan et al., 2007]. A^c itself is a function of the instantaneous average medium stiffness C . C is therefore computed in an iterative manner with the condition that the strain rate of the bulk medium equals the average over all the constitutive grains, weighted if necessary by the texture.

Macroscopic quantities such as material stiffness can be evaluated from this self consistent approach but for prediction of C^c in plastic regime, an appropriate theory of single crystal plasticity must be incorporated. In most cases the theory of [Hill, 1967] (concisely described by Raghunathan et al. [2007]) is used.

Slip, twinning and hardening in new EPSC scheme

In a given alloy, the plastic hardening behaviour is dictated by the activation and plastic flow of one or more slip systems. In the present mesoscopic/grain-level model, the hardening that results from dislocation-dislocation, dislocation grain boundary and dislocation-defect interactions are addressed phenomenologically by the evolution of the critical resolved shear stress (CRSS) for each slip system during deformation. A Vocé hardening law [Raghunathan et al., 2007; Clausen et al., 2008] is used. Akin to this, the activation of twins and their subsequent influence on other deformation modes are dictated using an extended Vocé hardening law

$$\tau^s = \tau_0^s + (\tau_1^s + \theta_1^s G) \left(1 - \exp \left(-\frac{\theta_0^s \Gamma}{\tau_1^s} \right) \right) \quad (\text{A.1})$$

where τ^s is the critical resolved (Schmid) stress, τ_0^s the initial critical resolved shear stress of the deformation mode and Γ is the accumulated shear strain. τ_1^s , θ_0^s and θ_1^s are fitting parameters that describe the asymptotic behaviour of each deformation mode. In addition, cross-hardening modes are included to account for, *e.g.* the effect of twins on hardening of other slip systems and forest hardening between slip systems. The model does not account for twin nucleation; they are assumed to nucleate through stress concentration mechanisms at the sub-grain scale that are unresolvable using this type of constitutive model.

In a self consistent scheme, the activation, growth and annihilation of twins is dealt with by a volume transfer from a parent grain to each potential ‘child’ twin orientation [Clausen et al., 2008]. The new child grain is incorporated into the Eshelby calculations, influencing the HEM properties, which in turn links to the global stress-strain response and the elastic strain in each orientation, which give rise to the measured elastic lattice strains along each texture fibre. A given parent grain is allowed to have multiple twin ‘children’, but it is restricted by the number of active systems. Further, continuity assumptions are applied for tractions and displacements

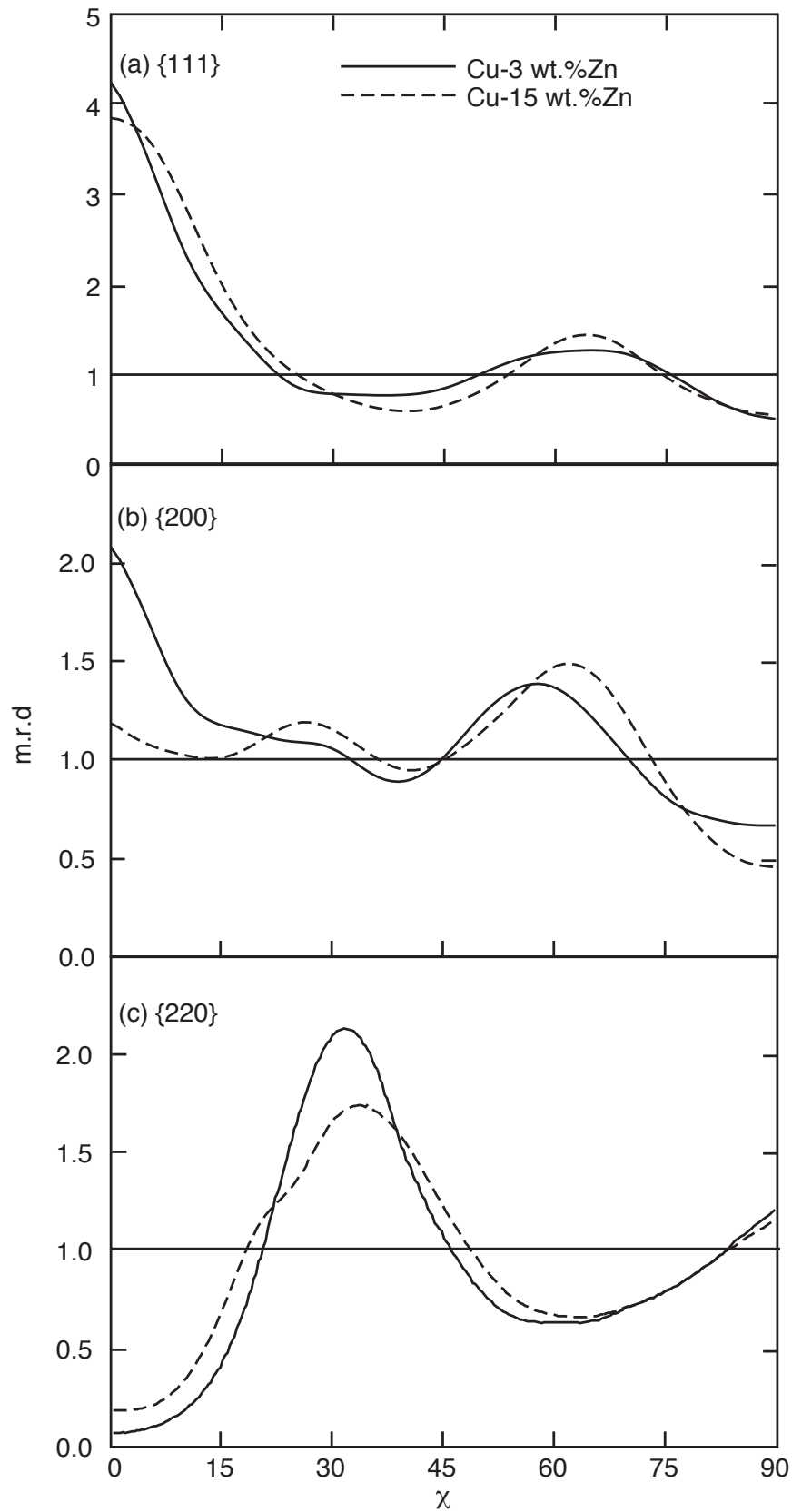


FIGURE A.3: Starting textures in the two alloys shown as the normalized intensity of the (a){111} (b){200} and (c){220} crystallographic planes as a function of subtended angle (χ) from the extrusion / longitudinal direction (tensile axis).

across the grain boundaries and it is assumed that elastic stress and strain components in the twin are equal to its parent. Also, the initial plastic strain within the twin is assumed to be same as that of the instantaneous plastic strain within its parent.

The extent of post-initiation growth of a twin can be defined, *a priori*, as a fraction f_0 of its parent grain [Clausen et al., 2008]. In polycrystalline alloys, the excess plastic shear is restricted by the compatibility stresses/backstress from the adjacent grains. These stresses are estimated by assuming that the plastic twin shear results in an equal and opposite elastic shear strain. An upper bound of associated stress relaxation is predicted by assuming that the grain in which twin appears is infinitely large and accommodates the twin shear elastically or elasto-plastically within itself. The stress on parent grain is then updated with the calculated back-stress, weighted over each twin fraction, to account for stress relaxation.

A.3 Results and Discussion

A.3.1 Experimental results: Texture, microstructure and tensile properties

The sample bulk textures were measured by neutron diffraction in an Eulerian cradle to obtain the $\{111\}$, $\{200\}$ and $\{220\}$ pole figures, Figure A.3. The normalised diffracted intensities average to 1 over all of orientation space, since the solid angle subtended varies with $\sin \chi$. The texture developed is predominantly $\{111\}$ fibre type as a result of extensive slip on $\{111\} <110>$ system and their resulting reorientation along the direction of extrusion for easy slip/shear. There is also a strong component of $\{200\}$ along this direction which normally results from dynamic and static recrystallization in *fcc* alloys. This component is much stronger in the Cu-3Zn alloy than in Cu-15Zn. The appearance of maxima and minima in the $\{220\}$ intensities at $\approx 30^\circ$ and $\approx 60^\circ$ reconfirms the existence of strong $\{111\}$ fibre texture in these alloys.

The microstructures observed are shown in Figure A.4a and b respectively. The average grain sizes evaluated by the linear intercept method are given in Table A.1 along with the compositions of the alloys measured using Energy Dispersive X-ray spectroscopy (EDX) in the SEM.

TABLE A.1: Grain sizes (μm) along (ED) and perpendicular (TD) to the extrusion direction, and the compositions (in wt.%) measured using EDX.

Alloy	ED	TD	Cu	Zn
Cu-3Zn	12.7	11.4	97.3	2.7
Cu-15Zn	12.5	10.6	85.2	14.8

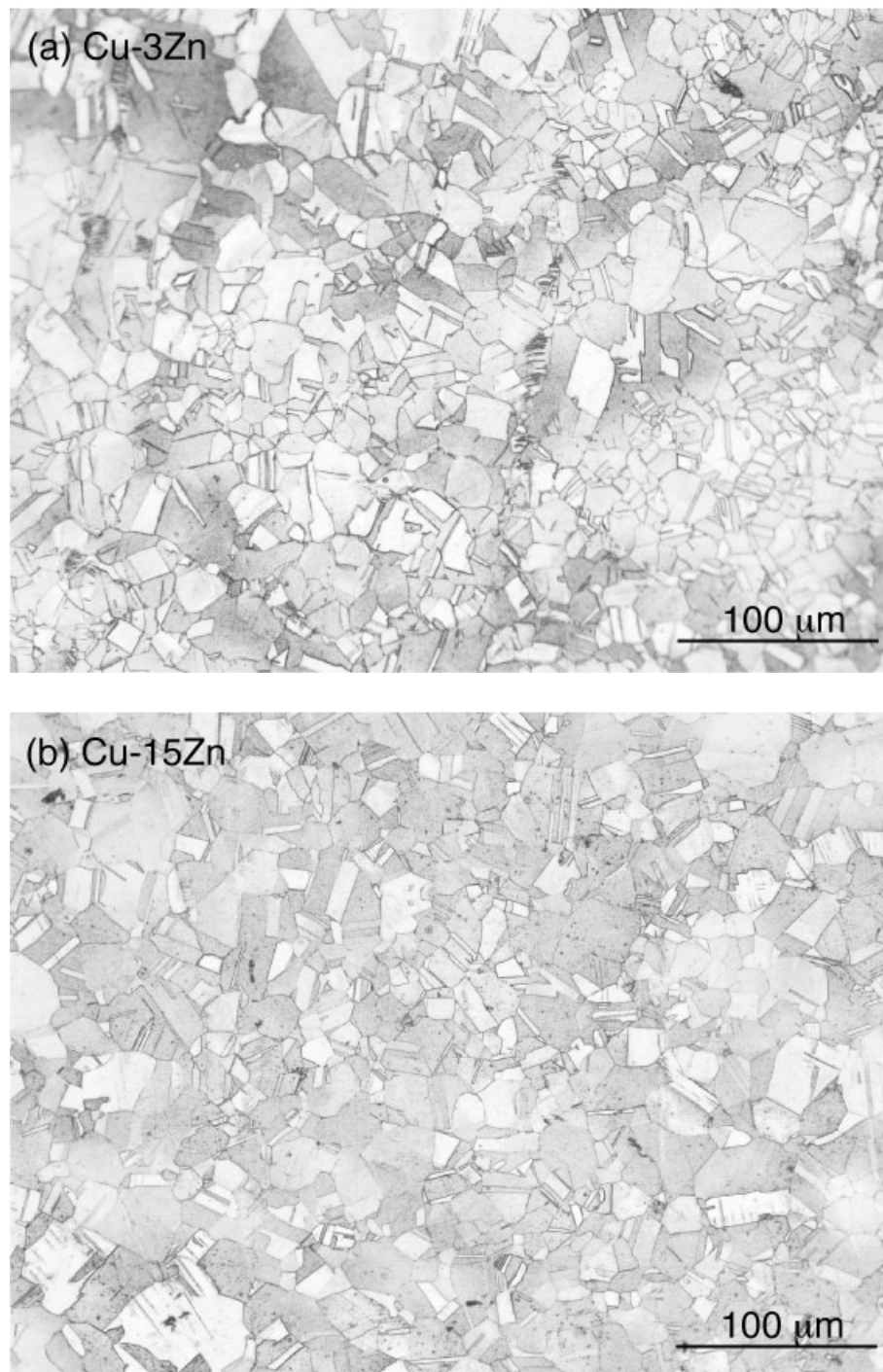


FIGURE A.4: Initial microstructure of (a) Cu-3Zn and (b) Cu-15Zn, viewed perpendicular to the extrusion axis.

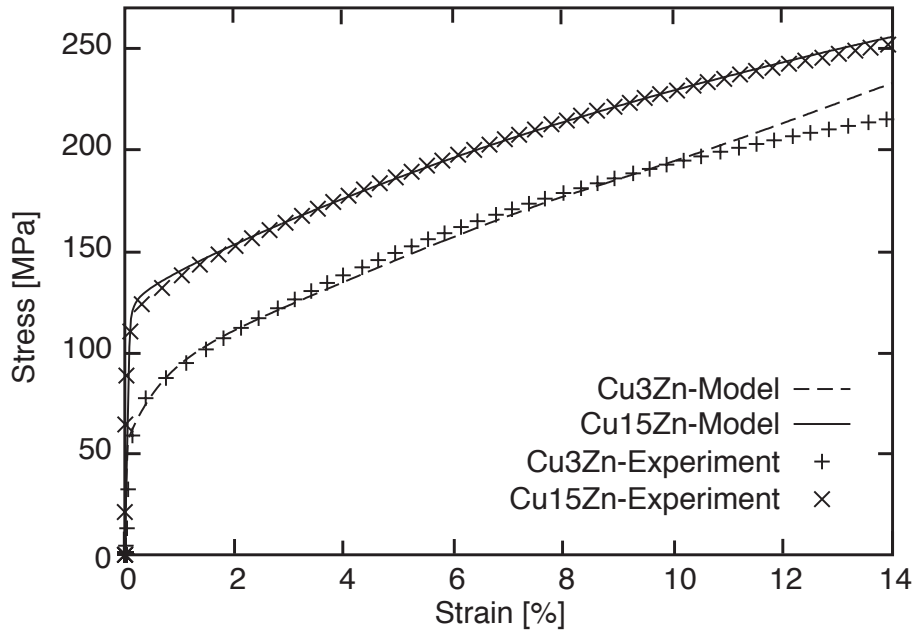


FIGURE A.5: Measured and simulated macroscopic stress-strain response in Cu-3Zn and Cu-15Zn.

The measured and predicted macroscopic stress-strain response of Cu-3Zn and Cu-15Zn alloys are shown in Figure A.5. The yield strength of Cu-3Zn was 60 MPa while Cu-15Zn yielded at 125 MPa. Addition of zinc reduces the stacking fault energy (SFE) and hence increases the tendency to twinning in brasses. During plastic deformation, these twins act as obstacles to movement of dislocations, increasing the flow stress, in addition to the normal solute hardening mechanism. Using $\sigma = K\varepsilon^n$, where K is initial yield stress and n strain hardening exponent, n was found to be 0.37 in Cu-3Zn and 0.29 in Cu-15Zn.

A.3.2 Modelling results

The ultrasonic measurements on single crystal α -brasses conducted by Rayne [Rayne, 1958] indicate that all the three elastic constants reduce with addition of Zinc. The single crystal elastic constants required for current calculations (Table A.2) were obtained by linear interpolation from [Rayne, 1958].

TABLE A.2: Single crystal elastic constants (GPa) used in the calculations, after Rayne [Rayne, 1958].

Alloy	C_{11}	C_{12}	C_{44}
Cu-3Zn	164.7	118.6	74.6
Cu-15Zn	152.2	110.9	71.7

TABLE A.3: Vocé hardening parameters in MPa for $\{111\} < 110 >$ slip and $\{111\} < 112 >$ twinning (labelled t) in Cu-3Zn and Cu-15Zn

Alloy	τ_0	τ_1	θ_0	θ_0	τ_0^t	τ_1^t	θ_0^t	θ_0^t	$\alpha = \tau_0^t/\tau_0$
Cu-3Zn	15	11	900	161	38	12	360	146	2.5
Cu-15Zn	42	15	200	100	54	22	220	103	1.3

The modelled macroscopic stress-strain response is shown in Figure A.5. Clearly, there is a good agreement between the measured and predicted response. The slip and twinning Vocé hardening parameters used in the current calculations are listed in Table A.3. The vulnerability of the alloys to undergo slip at a microscopic level on application of even small far field stresses is quite evident from the low τ_0 values. In Cu-3Zn, τ_0 is $\approx 4\times$ lower than its macroscopic yield strength while for Cu-15Zn alloy it is $\approx 3\times$ lower, which compares to the value of ~ 3 expected for randomly textured *fcc* polycrystals [Taylor, 1938]; of course, the present samples were textured so a exact value of 3 might not be expected. The increase in τ_0 with addition of Zn indicates the extent of solid solution strengthening and the ratio ($\alpha =$) τ_0^t/τ_0 reflects the relative ease of twinning compared to slip; as expected, Zn-alloyed Cu is more vulnerable to twinning. The analysis of Chin et al. [1969] suggests that Taylor polycrystals would undergo slip only when $\alpha > 1.15$, and twinning for $\alpha < 1.15$; in between these values slip and twinning will occur. In the present case, therefore, the Cu-3Zn alloy would be expected to deform largely by slip and the Cu-15Zn alloy by both mechanisms. In contrast, some deformations twins are observed in both alloys, Figure A.8.

In the elastic regime, the modelled elastic strain response of grains in the $\{111\}$, $\{200\}$ and $\{311\}$ diffraction orientations, termed the diffraction elastic constants (DECs) $E_{hkl} = \sigma/\varepsilon_{hkl}$ can be compared to those measured experimentally, Table A.4. The single crystal elastic constants, the texture and the compatibility stresses that develop during loading dictate the elastic moduli of individual planes; the comparison is observed to be reasonable, although not as good as is usually obtained where the C_{ij} are treated as fitting parameters.

In Figure A.6(a) and (b) the elastic lattice strain response of grains in the $\{111\}$, $\{200\}$ and

TABLE A.4: Experimental (e) and calculated (c) diffraction elastic moduli (in GPa) in Cu-3Zn and Cu-15Zn for $\{111\}$, $\{200\}$ and $\{311\}$ planes. $\Gamma = (h^2k^2 + h^2l^2 + k^2l^2)/(h^2 + k^2 + l^2)^2$

Peak	3Γ	Cu-3Zn			Cu-15Zn		
		e	c	c/e	e	c	c/e
$\{111\}$	1.00	132 $\pm$ 8	142	1.08	116 $\pm$ 14	150	1.30
$\{200\}$	0.00	70 $\pm$ 17	90	1.29	84 $\pm$ 6	94	1.12
$\{311\}$	0.47	96 $\pm$ 5	110	1.15	108 $\pm$ 5	115	1.06

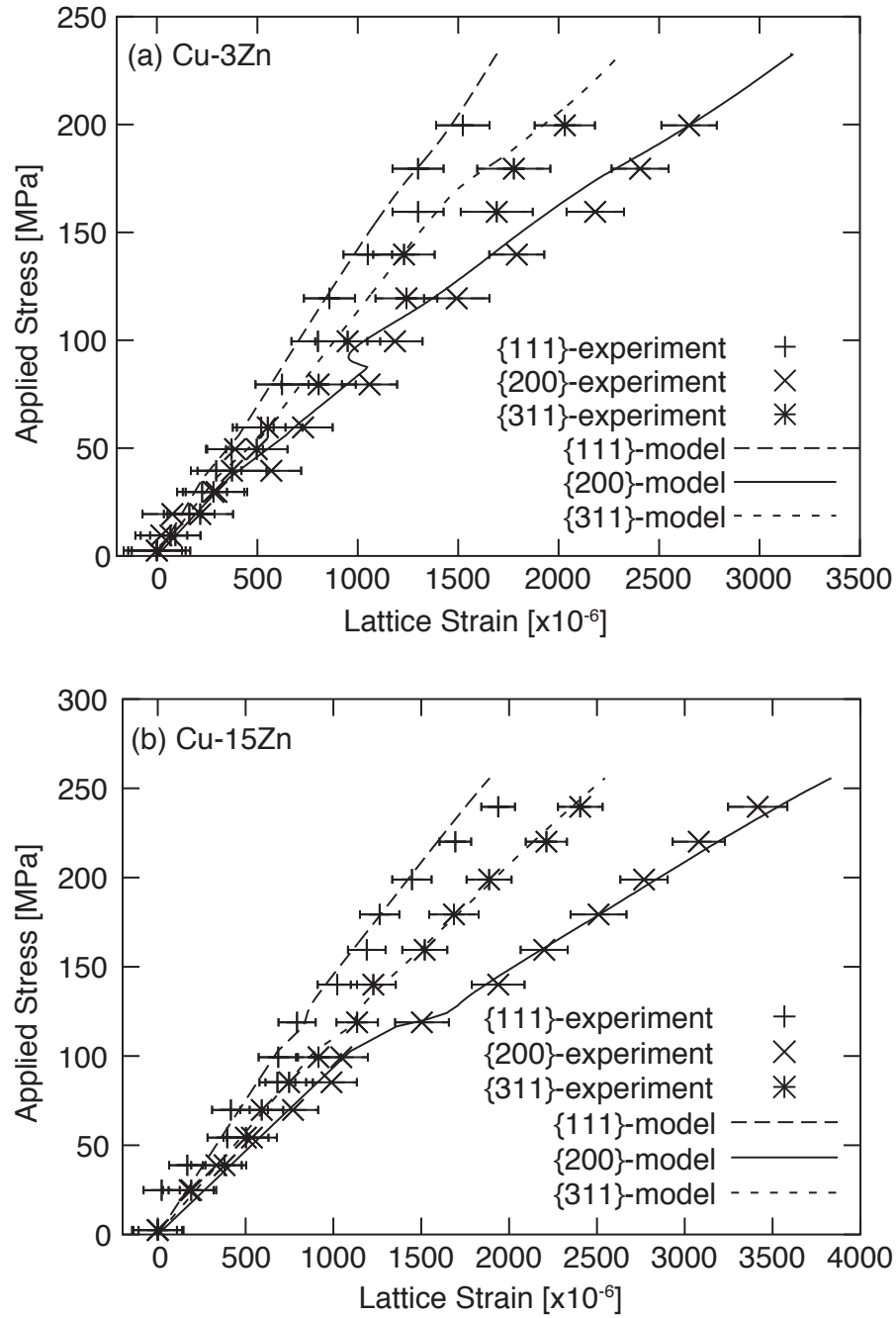


FIGURE A.6: The predicted and measured elastic lattice strain accumulation during loading on $\{111\}$, $\{200\}$ and $\{311\}$ in (a) Cu-3Zn and (b) Cu-15Zn alloys.

$\{311\}$ diffraction orientations along the longitudinal direction are shown. Again, there is a good agreement between the measured and simulated results. Any deviation from linearity is an indication of the onset of macroscopic yielding. Of the three crystallographic planes, the largest elastic strain is observed to accumulate on $\{200\}$ and the least on $\{111\}$. The load partitioning between the crystallographic planes observed here is similar to that predicted in randomly textured pure copper [Clausen et al., 1998]. The increase in elastic strain during the yielding transition at ~ 120 MPa on the $\{200\}$ plane in Cu-15Zn alloy is similar to that observed in pure copper and is indicative of a transfer of load from orientations that yield first to orientations that yield later in the elastic-plastic transition. In Cu-3Zn, the uncertainty in the lattice strains, combined with the low yield strain of the material, means that subtle changes in the lattice strain response could not be observed. However, the model predicts that for the Cu-3Zn alloy, the $\{200\}$ peak would be expected to undergo a negative lattice strain reversal at the onset of twinning (indicated by the arrow at 90 MPa and 1% plastic strain), whereas this is not predicted or observed in the Cu-15Zn alloy. Overall, therefore, the $\{111\}$ and $\{311\}$ peaks are observed to experience slight increases in lattice strain in the plastic regime, over and above those that would be expected from the elastic response. However, the $\{200\}$ peak is observed to experience significant increases in lattice strain in the plastic regime. Other orientations, not sampled experimentally, must therefore experience net decreases in lattice strain relative to the elastic line. The predicted residual strains in the unloaded state after 1, 5 and 10% plastic deformation are mapped over stereographic sections in Figure A.7, so-called strain inverse pole figures [Holden et al., 2002]. These depict, therefore, the distribution of residual elastic strains in the longitudinal direction that exist in the material as a consequence of plastic deformation. For clarity only strains in the longitudinal axis, *i.e.* along the extrusion or tensile loading direction are shown here. It is observed, as might be expected, that crystallographic planes that experienced lower (tensile) strains in the loaded state are then under compression after unloading. Most of the large tensile residual strains are concentrated near the $\{002\}$ pole; particularly on planes that lie in between $\{002\}$ and $\{113\}$. These strains reduce on moving further away towards $\{111\}$ and $\{220\}$; ending up predominantly compressive in the vicinity of $\{331\}$ and $\{531\}$. At all applied plastic strains, the corresponding residual strains in Cu-15Zn are larger in magnitude than those predicted in Cu-3Zn.

The (predicted) twinning behavior in both alloys is shown in Figure A.8. It is observed that twinning begins at the start of deformation in Cu-15Zn and that the rate of twinning decreases with plastic strain. Conversely, in Cu-3Zn there is no twinning initially and twinning only begins after $\sim 1\%$ strain. The rate of twinning is initially low but accelerates at around 5% strain, and at its maximum, accounts for around 9% of the deformation rate. However, it then exhausts at around 8.5% strain as the number of grains in a twinning orientation are exhausted and the rate

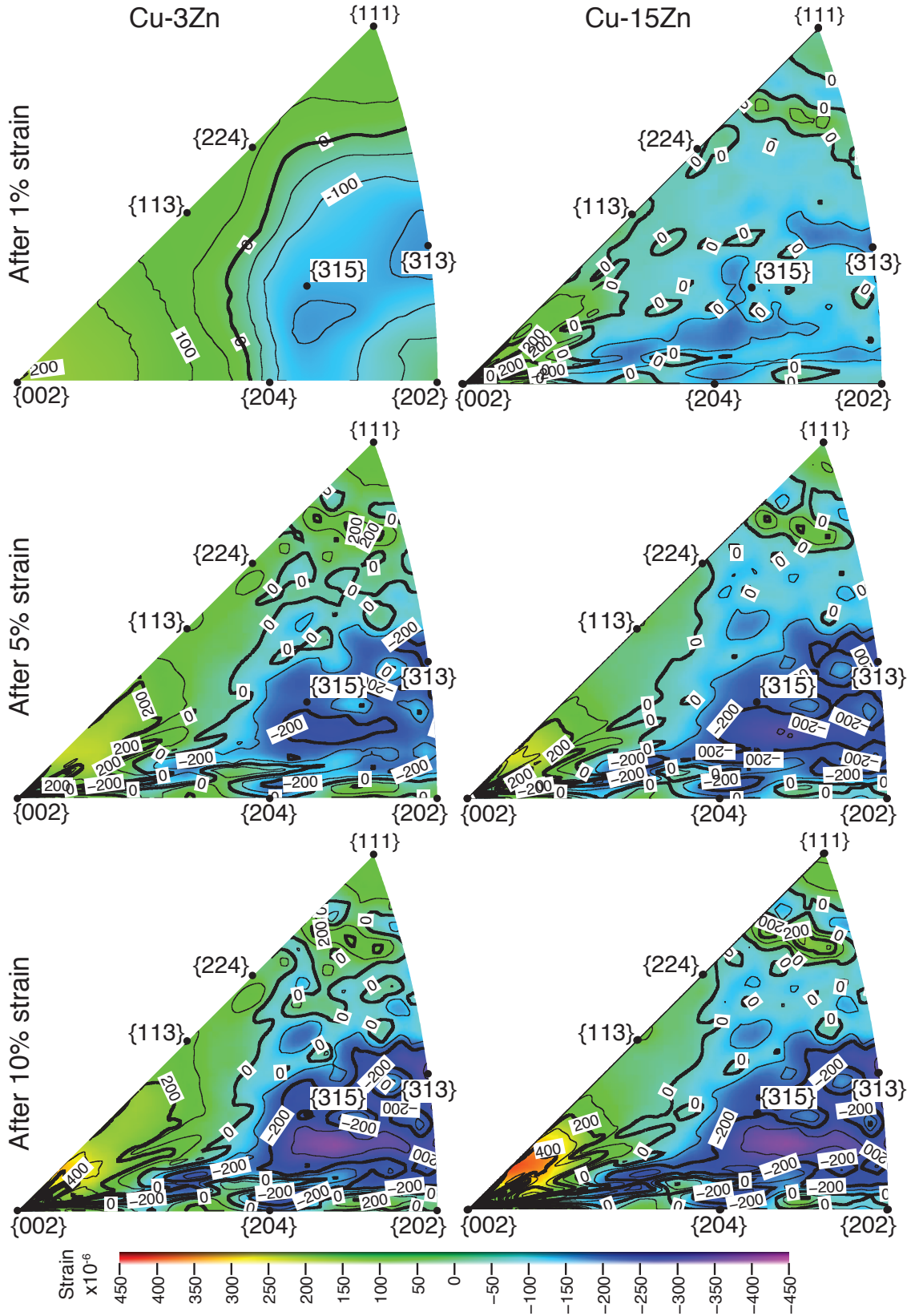


FIGURE A.7: Predicted residual elastic lattice strains in the longitudinal direction mapped in the inverse pole figure after unloading from 1, 5 and 10% plastic strain, respectively. Contours are drawn at lattice strain intervals of 100×10^{-6} and the 0, 200 and 400×10^{-6} contours are labelled.

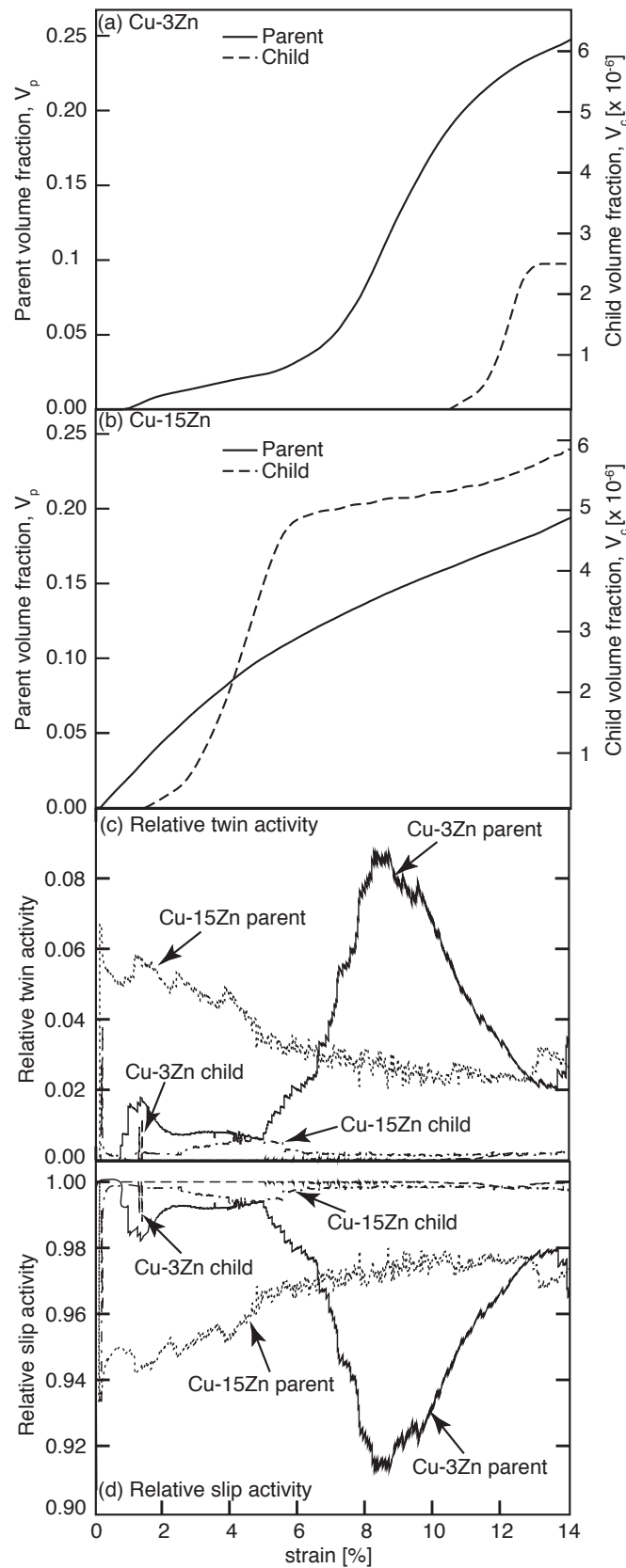


FIGURE A.8: Predicted evolution of twinning with plastic strain in the two alloys. (a) Cu-3Zn and (b) Cu-15Zn, the volume fraction of twins in the original grains ('parent') and the volume fraction of multiple twins ('child'). (c) relative twin activity and (d) slip activity in the two alloys, in the parent grains and in the twins.

of twinning then begins to reduce. In addition, in Cu-15Zn multiple twinning is observed, at a very low rate, almost from the start, but this only begins after around 9% strain in Cu-3Zn.

Of course, the extent of twinning will be affected by the fraction of grains that are originally in orientations favourable for twinning and unfavourable for slip. Therefore grains with their $\{111\}$ planes parallel to the loading axis are unfavourable for both $\langle 110 \rangle \{111\}$ slip and $\langle 112 \rangle \{111\}$ twinning, which compose a significant fraction of the extrusion texture. Therefore the total amount of twinning observed in these samples must be limited. However, the textures and grain sizes of the two samples were very similar, and so it must be concluded that the increased level of twinning inferred from the intensity evolution and model predictions must be due to the increased Zn content, *i.e.* the lower stacking fault energy. These observations are also empirically consistent with the microstructures observed after deformation.

The present modelling approach is simplistic in that the twin interface energy, growth and interaction of twin lamellae are not addressed. It has been shown [Leffers and Bildsorensen, 1990] in rolled Cu-15Zn brass that the $\langle 112 \rangle \{111\}$ twins formed are not homogeneously distributed within the grain but that they segregate into lamellae separated by layers of matrix material, with the interface planes parallel to a particular $\{111\}$ plane. Therefore the extent to which the present model can hope to reproduce the complete microstructure must be limited. However, the overall diffraction averages of the diffracted intensity and elastic strain in grains satisfying the diffraction condition are largely reproduced.

A.4 Summary and Conclusions

The evolution of elastic lattice strain and texture during the deformation of two α -brasses, Cu-3Zn and Cu-15Zn, has been examined. The higher Zn containing alloy was stronger and having a lower stacking fault energy, was more susceptible to twinning. The micromechanical behaviour was modelled using a recently-developed elastic-plastic self consistent modelling (EPSC) scheme [Clausen et al., 2008] that has previously only been applied to pure hexagonal metals. The following conclusions can be drawn.

1. For a given applied stress, the variation in the elastic lattice strains increases with Zn content. Consequently, the residual lattice strains predicted after unloading also increase with Zn content. Their distribution remains broadly similar and they increase with plastic strain. The largest residual strains are predicted in grains near- $\{002\}$ relative to the loading direction, at around 4.5×10^{-4} in Cu-15Zn and the smallest around around -3×10^{-4} near the $\{531\}$ pole. These correspond to quite large residual stresses (on the order of 1/3rd of the yield stress).

2. Significant amounts of twinning, up to around 25%, are predicted in both alloys. Twinning begins at the start of plastic deformation in Cu-15Zn, but only after around 1% strain in Cu-3Zn.
3. The present model appears to be able to predict the effect of twinning on the lattice strain evolution reasonably accurately. It does not account for lattice rotation during slip.

Appendix B

In situ observation of individual variant transformations in polycrystalline NiTi

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In situ observation of individual variant transformations in polycrystalline NiTi

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The transformation behaviour of the individual texture components of NiTi rolled sheet was examined by synchrotron X-ray diffraction. The diffraction measurements performed in this study only captured a small fraction of orientation space, allowing the transformation of individual orientations to be studied. It was found that the individual B2 orientations transform at distinct points in the load plateau and that this can be correlated with the appearance of individual B19' variant orientations.

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Keywords: Shape memory alloys (SMA); Synchrotron radiation; Martensitic phase transformation; Texture; Variant selection

NiTi-based shape memory alloys are of great current interest in the aerospace industry as potential candidates for replacing mechanical actuators. The operating principle is to exploit the phase transformation to achieve a change in shape of the sample, which occurs due to a combination of temperature and stress. In NiTi the high-temperature austenite phase is an ordered B2 structure, whilst the low-temperature phase is monoclinic B19' martensite. These two phases have been shown [1–3] to possess a $\{110\}_{B2} \parallel (002)_{B19'}$ or $\{110\}_{B2} \parallel (111)_{B19'}$ orientation relationship. It is possible for an intermediate phase to form during the transformation pathway, either R or B19, depending on the prior thermomechanical processing or alloying additions [4]. The understanding of variant selection processes during deformation is critical to the successful modelling of phase transformations [5–8].

Previous researchers [9] have shown using microscopy that the transformation is progressive within a single grain, proceeding via the selection of twin-related variants that accommodate the imposed strain along the tensile axis and also self-accommodate the off-axis transformation strains [10–12]. Also, before-and-after texture analysis has shown [13], at least empirically, how the texture evolves during loading to the B19' state and unloading back to the B2 phase. Finally, Vaidyanathan and co-workers [14–18] performed in situ neutron

diffraction using the large area detectors at NPD and SMARTS and showed that, measured over a large fraction of orientation space, the transformed volume fraction varies with the overall transformation strain in the load plateau region.

In this paper, results of a synchrotron diffraction study carried out at the European Synchrotron Research Facility (ESRF) are presented. These are used to examine the progress of the transformation for a small fraction of orientation space, allowing the observation of the transformation of an individual component of the starting B2 texture.

Dogbone-shaped tensile specimens of NiTi sheet were loaded in tension at room temperature using a FaME38 electro-thermomechanical tester while in situ X-ray synchrotron diffraction was performed on the ID15B beamline at ESRF. Figure 1a shows a side view of the diffraction geometry. Diffraction patterns were collected every 4 s using an incident X-ray wavelength of 0.1415 Å and a Pixium area detector. The diffraction rings collected (Fig. 1b) give information about the response of grains satisfying the Bragg condition, with $\psi = 0^\circ$ corresponding to the tensile axis of the test, also the rolling direction (RD) of the sheet and $\psi = 90^\circ$ corresponding to the normal direction (ND) of the rolled sheet employed. The rings were segmented into 10° regions using the software program FIT2D [19]. Peaks were indexed using GSAS [20] (Fig. 1c). R-phase as well as the expected B2 phase was determined to be present at the beginning of the test. The diffraction spectra were fitted

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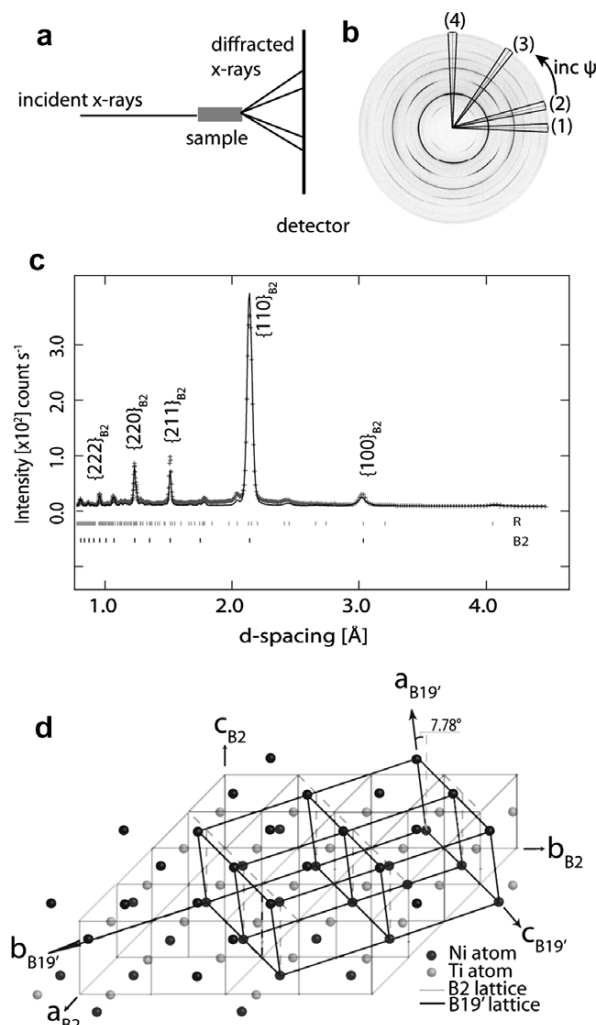


Figure 1. (a) Schematic (side view) of the diffraction geometry. (b) Resultant Debye–Scherrer diffraction rings at the beginning of the test. Azimuthal segments indicated are (1) $-5^\circ < \psi < 5^\circ$ (RD), (2) $15^\circ < \psi < 25^\circ$, (3) $55^\circ < \psi < 65^\circ$ and (4) $85^\circ < \psi < 95^\circ$ (ND). (c) Synchrotron diffraction spectrum of the starting sample. (d) The unit cell relationships between the B2 and B19' phases.

using a peak-fitting script developed by S.S. Babu. These fitted intensities were subsequently normalised for each phase; Figure 1d shows a schematic of the predominant orientation relationship between the B2 and B19', i.e. $\{110\}_{B2} \parallel \{110\}_{B19'} \parallel (002)_{B19'} \parallel (002)_{B2}$.

The changes in intensity around the diffraction rings in Figure 1b give an indication that a rolling texture is present in the NiTi sheet. The B2 phase is expected to deform by $\langle 111 \rangle$ slip and pencil glide, and therefore this observed texture is not unreasonable.

The measured composition of the sample tested was found to be 52.9 at.% Ni, 47.1 at.%Ti with 0.05 at.% O. The transformation temperatures were measured using differential scanning calorimetry (DSC) and the A_f and M_f temperatures were found to be ~ 50 and -80°C , respectively.

In Figure 2 the macroscopic stress–strain response of the NiTi is shown. The shape memory behaviour

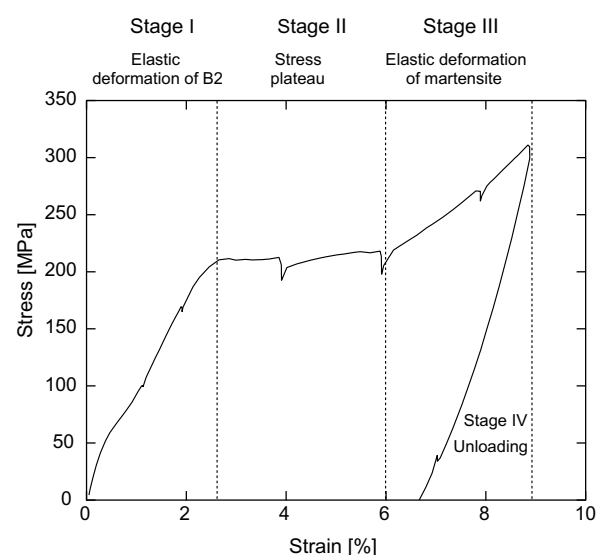


Figure 2. Macroscopic stress–strain response of NiTi. Stage I represents in initial elastic loading of the B2 phase; Stage II indicates the stress-plateau regime; Stage III is the regime for martensitic elastic deformation; and Stage IV is unloading at the end of the test.

observed is as expected: an initial elastic regime until a strain of $\sim 2.2\%$ followed by a stress plateau regime until a strain of $\sim 6\%$. The stress was then increased to 300 MPa before unloading. The sample did not show complete strain recovery as the test temperature was lower than A_f [21]. The load drops correspond to position holds during the test.

Figure 3 shows the spectral evolution in the d -spacing range of 1.9–2.4 Å at the selected azimuthal segments shown in Figure 1b and Figure 4b shows the evolution of the fitted normalised intensities. In general, the intensities of the B2 and B19' show a gradual change initially in Stage II, clearly evident in Figure 4b, culminating with a sudden change in intensity at the end. Along the RD in the plateau regime, the intensity of $\{110\}_{B2}$ peak does not change substantially until the end of the stress plateau where a large decrease is observed. At the same point in the measurement sequence the intensity of $(002)_{B19'}$ increases suddenly in the RD. Along the ND, the initial $\{110\}_{B2}$ intensity is lower compared to that of the RD. During Stage II the $(020)_{B19'}$ peak appears as a shoulder at the expense of the $\{110\}_{B2}$ peak. In Figure 3c ($55^\circ < \psi < 65^\circ$ from the RD), the appearance of the $(012)_{B19'}$ peak is observed during Stage II as well as a small fraction of $(002)_{B19'}$. However, at $15^\circ < \psi < 25^\circ$ from the RD (Fig. 3d), the appearance of the $(11\bar{1})_{B19'}$ is observed. For the $(111)_{B19'}$ and $(012)_{B19'}$ peaks, it was not possible to determine which parent B2 variants they transformed from, purely due to the small region of the orientation space being measured.

The diffraction measurements performed in this study only capture a small fraction of orientation space lying along the periphery of the overall texture pole figure due to the low intrinsic divergence of the synchrotron beam utilised ($< 1^\circ$). This allows the transformation of individual orientations in the polycrystal to be studied,

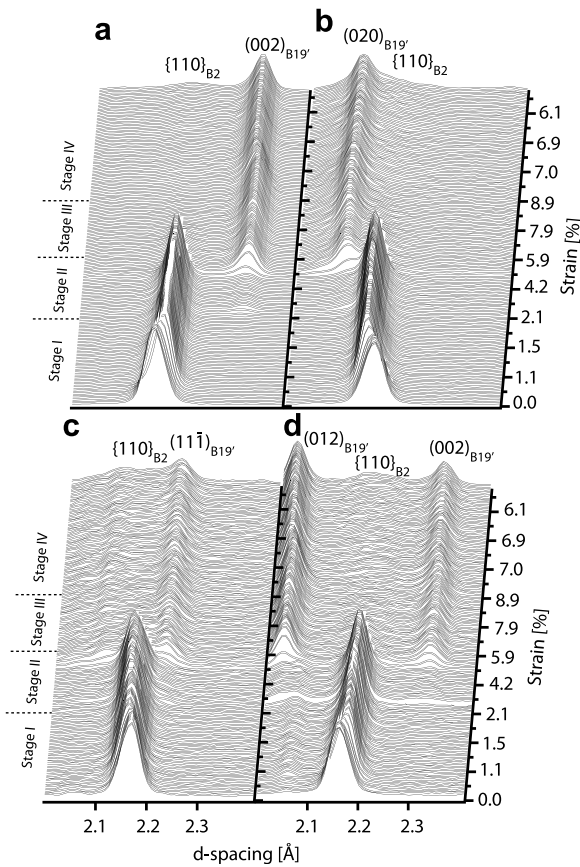


Figure 3. Evolution of d -spacing with strain in (a) the rolling direction (RD), (b) the normal direction (ND), (c) $55^\circ < \psi < 65^\circ$ from the RD showing the $(11\bar{1})_{B19'}$, and (d) $15^\circ < \psi < 25^\circ$ from the RD showing the $(012)_{B19'}$.

giving information on the evolution of lattice spacing (due to elastic strains) and the volume fraction (intensity). Figure 4a shows the major poles of an individual B2 grain possessing the primary rolling texture and a B19' variant with the $(1\bar{1}0)_{B2} \parallel (002)_{B19'}$, $(110)_{B2} \parallel (020)_{B19'}$ orientation relationship. This variant type appears to be consistent with the observation of a simultaneous increase in the RD $(002)_{B19'}$ and ND $(020)_{B19'}$ and a decrease in the ND and RD $\{110\}_{B2}$.

The observation of transformation of the dominant texture component, the RD $\{110\}_{B2}$, only at the end of the plateau might be rationalised in the following way. An individual B2 grain would be expected to transform when the resolved shear stress on the invariant plane reaches a critical value. It would be expected that the grains with highest resolved shear stress would transform first, accommodating the applied strain. Less favourably oriented grains would only transform once the transformation has completed in more favourable orientations. In order to examine this proposition, the evolution of elastic lattice strain in each phase is shown in Figure 5.

However, load shedding to the RD $\{110\}_{B2}$ is not observed until the very end of the plateau (Fig. 5a), although the $(002)_{B19'}$ does show a gradual increase in d -spacing and therefore load (Fig. 5c). Similarly, the

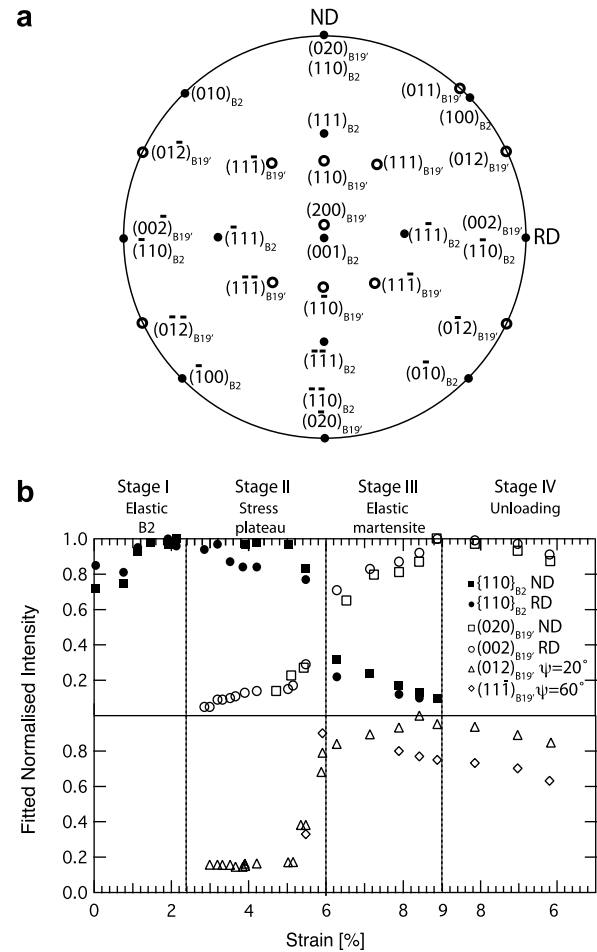


Figure 4. (a) Orientation relationship and pole locations [22] for the RD $(1\bar{1}0)_{B2} \parallel (002)_{B19'}$, ND $\{110\}_{B2} \parallel (020)_{B19'}$ transformation. (b) Evolution of intensity of selected peaks and orientations during the loading sequence, normalised by the maximum observed for each peak/azimuthal segment.

large increase in $(002)_{B19'}$ intensity and decrease in RD $\{110\}_{B2}$ at 5.4% strain is not initially accompanied by a change in the elastic strain (d -spacing) in either peak (Fig. 5). However, once the transformation is exhausted a significant jump in d -spacing is observed in the RD $(002)_{B19'}$. Elastic loading of the remnant B2 and majority B19' phase is then observed in the Stage III regime, during which the final remnant RD $(110)_{B2}$ transforms. No reversion of the B2 phase is observed during Stage IV unloading, as expected, although a drop in intensity is observed in the martensite phase, which can be attributed to elastic lattice rotation away from the Bragg condition.

Therefore one can infer that a transforming orientation accommodates the applied strain increment completely, without shedding load onto untransformed orientations. Thus, each orientation appears to transform in isolation. As the transformation exhausts in some orientations, it is then taken up in less favourable orientations, without increase in their load.

It is concluded that it is possible to observe individual B2 orientations transform at distinct points in the load

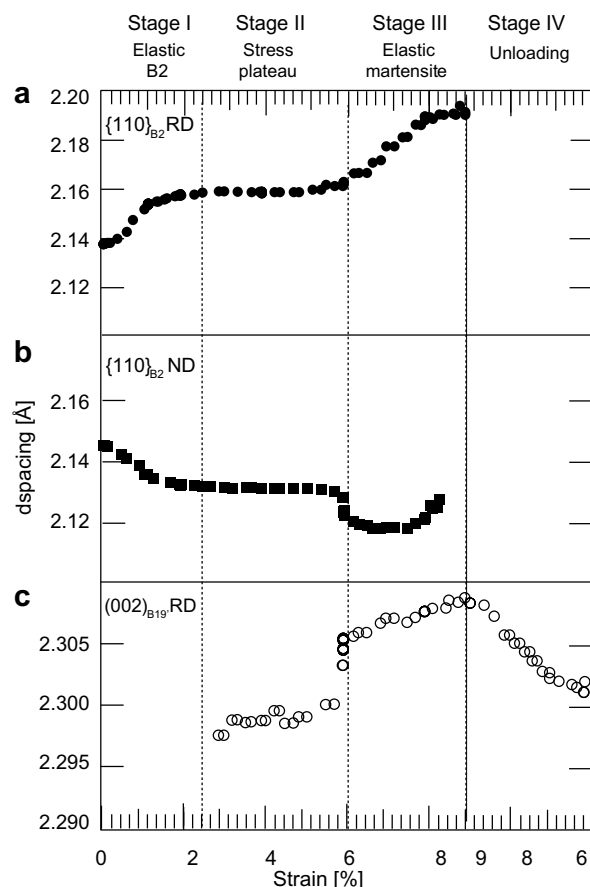


Figure 5. Evolution of interplanar spacing with bulk strain for (a) $\{110\}_{B2}$ (RD), (b) $\{110\}_{B2}$ (ND) and (c) $(002)_{B19'}$ (RD).

plateau. The transformations occurs suddenly at a strain of $\sim 5.5\%$ and this can be correlated with the appearance of individual B19' variant orientations. Therefore, at the level of individual orientations, the transformation is not continuous and proportional to the applied strain, as observed by Vaidyanathan and co-workers [14] when observing large fractions of orientation space collectively. In addition, the strain measured in individual orientations does not appear to change significantly during the majority of the stress plateau region, which implies

that transforming orientations do not shed load onto untransformed orientations.

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